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ORIGINAL PAPERS

AN EIGHTEEN MONTHS' HIGH TEMPERATURE TEST ON REFRACTORY TEST SPECIMENS

Frank H. Riddle[1] and Albert B. Peck[1]

ABSTRACT

Advantage was taken of an eighteen months' continuous run of the Dressler kiln of the Champion Porcelain Company firing to cones between 17 and 18, to observe the effect of the temperatures and the gas conditions in various parts of the kiln upon a large number of standard bodies and experimental mixes.

The kiln and conditions within it are briefly described, as well as the types of bodies used.

The observed changes in outward physical properties of the bodies are supplemented by petrographic-microscopic examinations in order to determine or explain the reasons for the behavior of the bodies.

Three instances of the production of deposits of artificial minerals formed in the kiln during firing are also described and explanations for their occurrence are given.

Introduction

At the time the Dressler Kiln of the Champion Porcelain Company was shut down in June, 1924, it had been in continuous operation for a period of eighteen months in firing ware at cones 17 (1490°C) to 18 (1510°C) and occasionally even higher.

Before the kiln was lighted for this long run it was thought advisable to place a number of standard bodies and experimental mixes in various parts of the kiln with a view of observing the effects of various gas conditions as well as temperatures.

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[1] Research Laboratories, Champion Porcelain Company. Recd. October, 1925.

So far as the writers are aware, this is the first instance of experimental work being deliberately conducted under such conditions of long time at such high temperatures. The actual pyrometer temperatures to which the bodies were exposed cannot be definitely stated for the reason that the bodies were in the port holes, or behind or within the muffles, while the pyrometers were located along the crown of the kiln. The latter, however, showed a range from 579°C to 1462°C. The actual temperature of the bodies opposite a pyrometer was undoubtedly higher in all cases and in some instances much higher.

Even though actual temperatures cannot be stated definitely, the resulting effects on these experimental bodies were in some instances so interesting that it was thought they might also be of interest to others. It is the purpose of this paper at a later point to present results both from the standpoint of the physical and petrographic-microscopic changes involved.

The Kiln

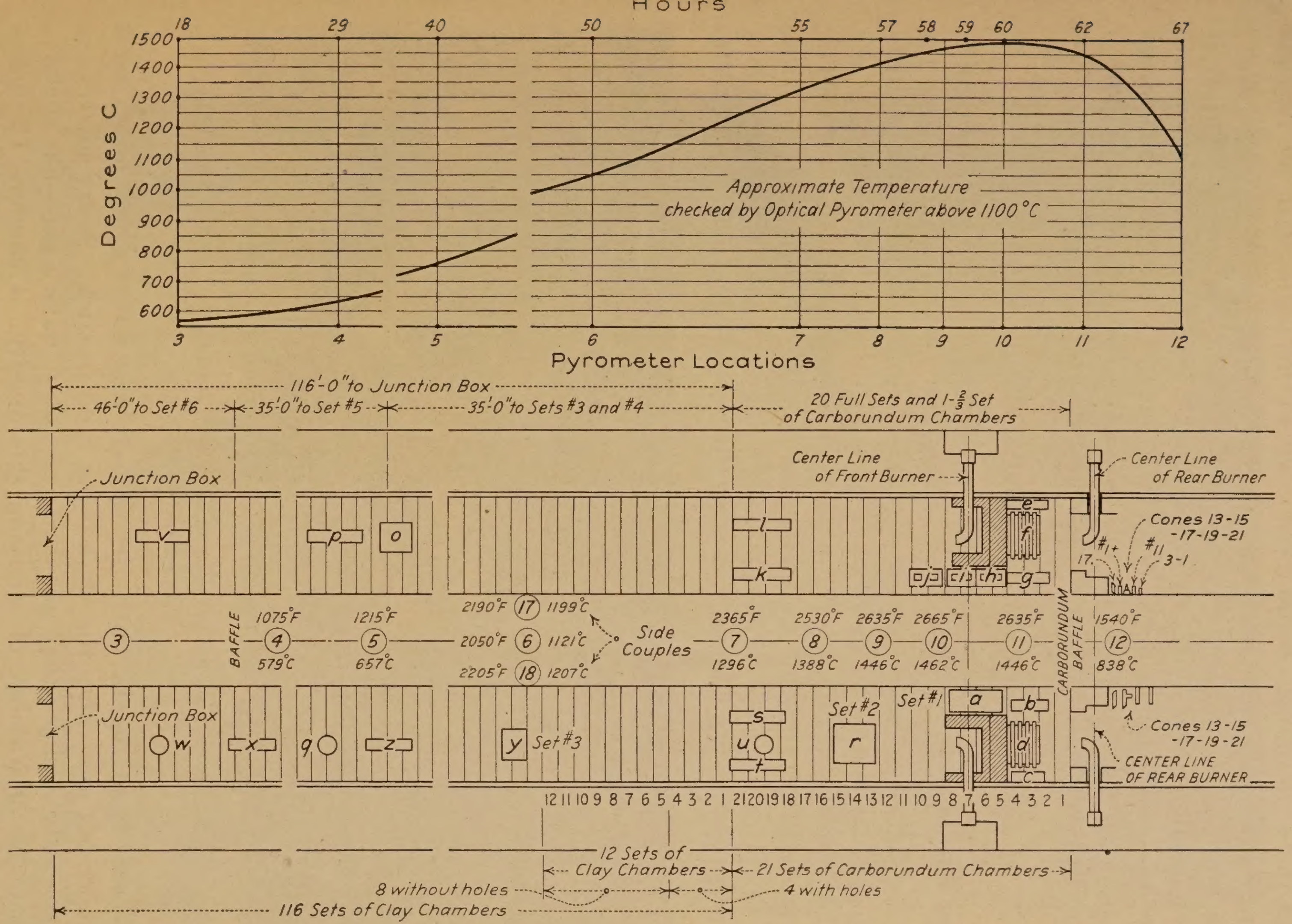
The Dressler kiln is, in general, similar in construction to the standard form of Dressler muffle kilns. On account of the extreme temperatures, great care was used in the selection of the refractories and the type of construction. Perhaps the two most unusual parts of the construction are the silica brick crown and silicon carbide brick damper boxes at the head end of the combustion chambers, through which the super-heated air is drawn down into the chambers for combustion.

The kiln, which is approximately 312 feet long, has combustion chambers approximately 140 feet from damper boxes to junction boxes where the products of combustion are drawn out to the stack.

Of the chambers, 21 sets or 21 feet are of very refractory high grade, shiplap-jointed silicon carbide, cemented together with a pure grade silicon carbide mixture containing a small amount of clay bond.

The silica brick crown extends for approximately 75 feet from the edge of the damper box along over the silicon-carbide chamber section. The balance of the crown is made of high grade clay brick.

Figure 1 shows a general layout and the positions of the various test specimens in the kiln. Unless otherwise mentioned, the only specimens of particular interest in the present case are those placed in the combustion chambers. The distance-temperature curve shown in Fig. 2 is the curve of the temperatures shown by thermocouples in the kiln crown. These would necessarily be somewhat lower than the combustion chamber temperature on account of the lag due to transfer of heat through the chambers. The gas analysis in the combustion chambers



FIGS. 1 and 2. Diagram of Dressler tunnel kiln showing the position of the various specimens and approximate temperatures indicated by the thermocouples in the crown.

may also vary considerably from the gas analysis in the ware firing tunnel. Substantially pure air is drawn down through the damper boxes from the ware tunnel. From a point where this unites with the fuel gas from the burners down through the combustion chambers to the junction boxes the atmosphere varies from slightly oxidizing or neutral at the burners to more oxidizing at the junction boxes. The chambers are, of course, under minus pressure. This is bound to result in some leakage of air into the chambers and thus brings about an increased oxidation as the gases progress down through the chambers.

Silicon-Carbide Cylinders and Sag-Bars

Test Specimens Silicon-carbide specimens were made up with a view of studying suitable mixtures for saggers for use in this particular factory. As a result the field was necessarily limited and hence may not be of general interest. A sagger for the work in question must show no signs of deformation at cone 20. The sagger walls are under compression while the bottoms have to withstand a sagging due to the load of ware. This puts the bottoms under a compression on the upper side and tension on the lower side. The mixtures must also be fairly dry or free from fluxes which might tend to bore out and cause the ware being fired to stick. A dry mixture is more easily oxidized than one dense enough to have a glass-like surface, hence the desirability of studying this quality. Cylinders 1½ inches in diameter by 1½ inches high were selected for this test while bars 8 inches long, 2 inches wide and ½ inch thick were selected for the sag test. These were supported on knife edges placed approximately six

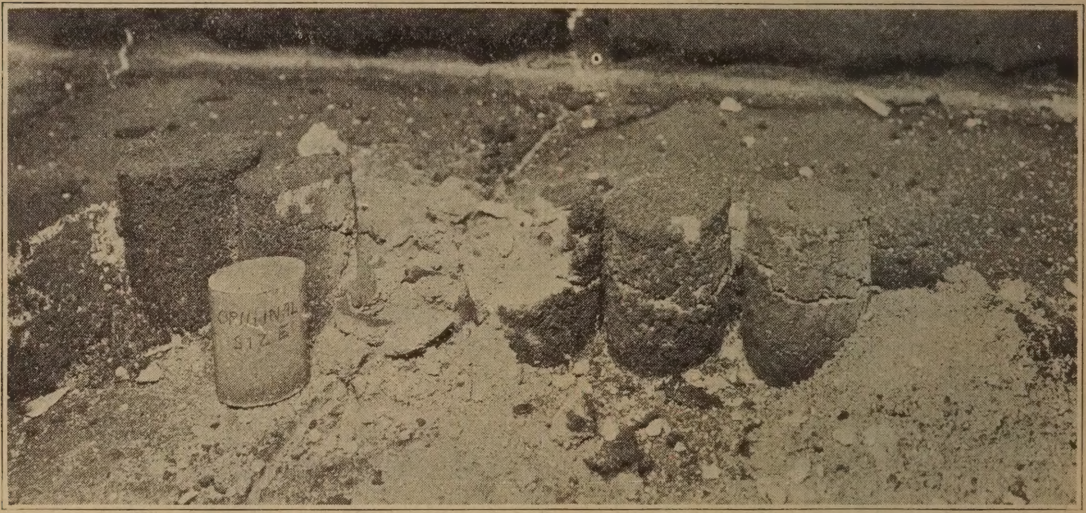


FIG. 3. Silicon-carbide cylinders at about 600°C. Note the amount of swelling and disintegration.

inches apart. It was not necessary to place sag bars in any but the hottest parts of the kiln as sagging is only brought about by softening of the bond. These sagger mixtures depend on grain size for density and the denser ones are, of course, more difficult to oxidize than the more open-grained ones.

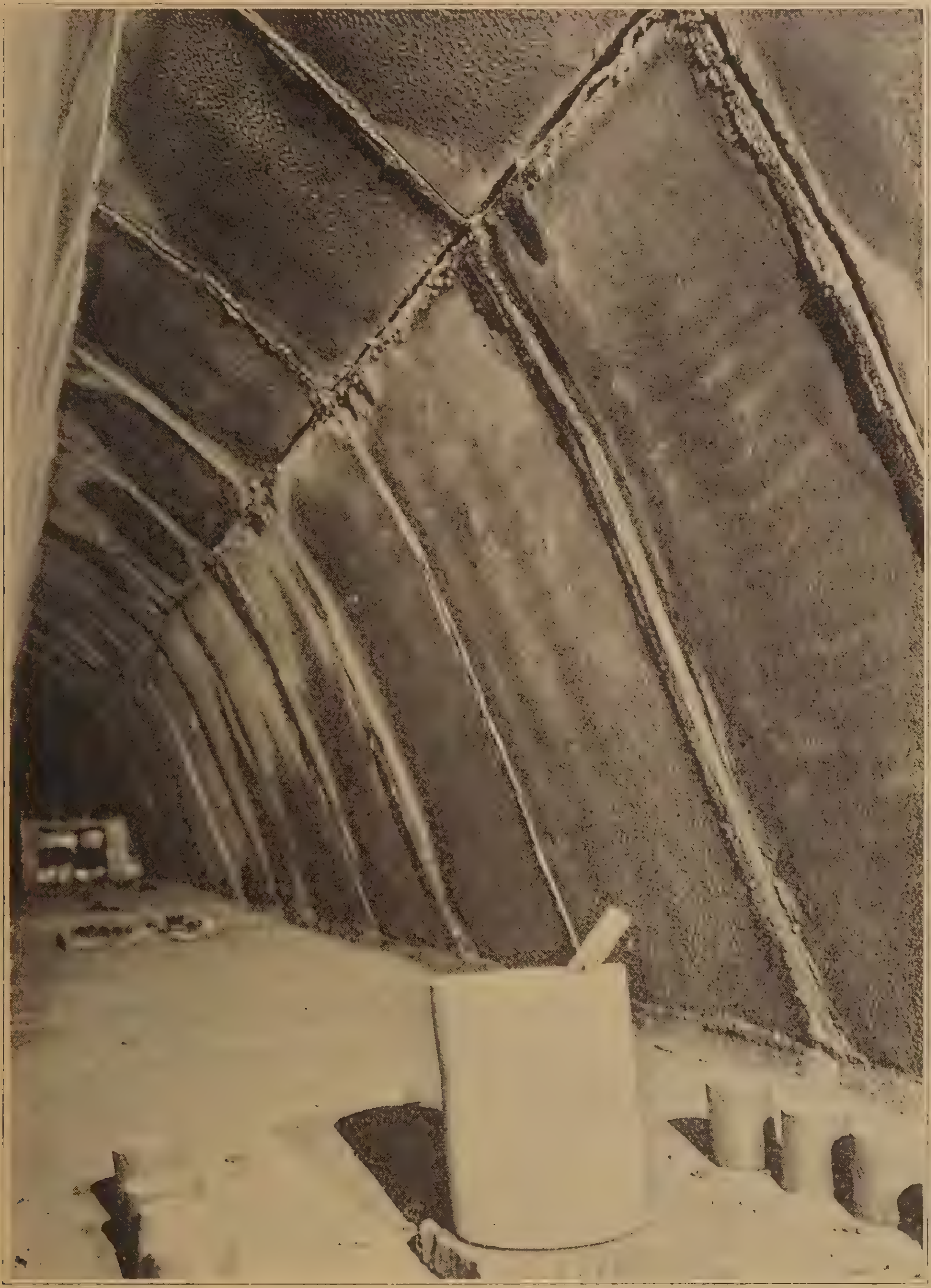


FIG. 4. Silicon-carbide cylinders at about 1200°C. Swelling and disintegration is not as marked as in Fig. 3.

These silicon-carbide specimens proved to be among the most interesting of the test pieces taken from the kiln, covering as they did the whole range of temperatures existing in the kiln from a minimum of approximately 579°C to a maximum of above 1462°C.

Swelling and disintegration or dusting to degrees varying from partial to complete was a rather characteristic phenomenon. This was especially true at low to intermediate temperatures. At the higher temperatures it was not so prominent, although in some cases the specimens almost completely volatilized. Thus at the lower temperatures (about 600-1000°C) most of the specimens swelled to nearly twice their original size and dusted (Fig. 3). Some Fe_2O_3 gave a red or brown color to the specimens. At intermediate temperatures (about 1320°C) the bodies were firmer and also showed more or less Fe_2O_3 both externally and internally (Fig. 4). The outer surfaces presented a slightly glazed appearance. The interiors were always some shade of gray and the color was generally roughly proportional to the fineness of grain of the original silicon carbide. The lightest of all was a body which was composed entirely of new silicon carbide over half of which was finer than 65-mesh. At the highest temperature (1446°C+) the bodies were in front of the rear burner and in the muffles opposite the hot zone (Fig. 5). The temperature can only be indicated as above 1446°C. Swelling was not so apparent at this point but volatilization was very prominent. Two bodies containing 10% of clay had almost completely disappeared or changed to cristobalite. Many others showed only a hollow shell remaining.

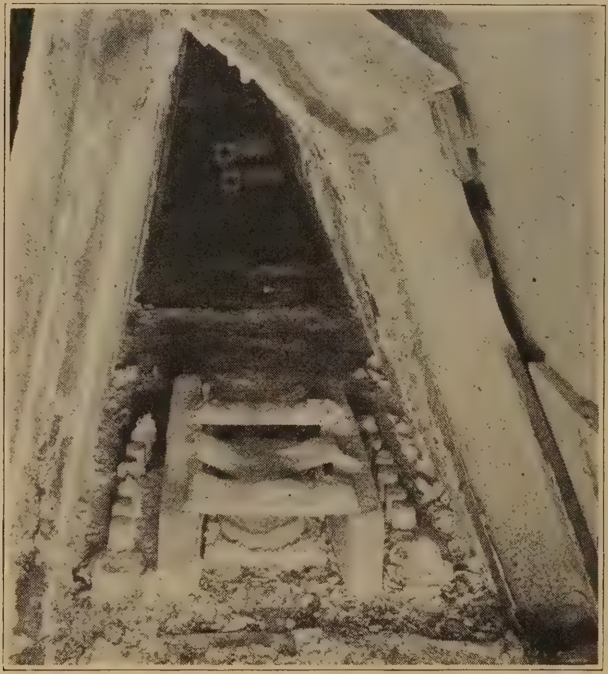


FIG. 5. Silicon-carbide cylinders and sag-bars just in front of the forward burners. Temperature 1462°C+. The specimens have swelled and volatilized and are white due to a coating of cristobalite. Note the round craters or lithophysae both on the specimens and along the lower and upper joints of the muffles.

Petrographic examination showed several interesting facts and reasons for the behavior of the bodies. The most prominent new constituent formed was cristobalite. In low temperature specimens this occurred as minute grains or aggregates in which silicon carbide was embedded.

The cristobalite grains themselves very frequently showed numerous minute inclusions of bubbles. Although it cannot be definitely stated, it seems probable that these are CO_2 bubbles, the gas resulting from the oxidation of the silicon carbide having been entrapped when the cristobalite was formed as a result of the same action.

Specimens from points of intermediate temperatures showed the same sort of cristobalite. These specimens showed some vitrification due perhaps to both the higher temperature and the presence of a little Fe_2O_3. The light color of the interiors was due to the formation of cristobalite and the amount seemed to be governed by the amount of fine silicon carbide originally in the body. Fineness of grain appeared to encourage the formation of cristobalite.

In the high-temperature specimens, cristobalite was again very prominent, in fact, in some the amount of silicon carbide remaining was almost negligible. Usually the cristobalite was pure white and distinctly vitreous. Microscopically it showed much larger crystals of better development than in the lower temperature specimens. Gas inclusions were much less common at these temperatures, doubtless because so much cristobalite itself had been volatilized as well as CO_2.

Mullite ($3\ Al_2O_3.2\ SiO_2$) was found in varying amounts in nearly all specimens at all temperatures. In some its presence was due to the use of clay in the body. In others where no clay was used, it must have come in as an impurity.

The cause of the formation of the cristobalite in these cylinders must be due to oxidation of the silicon carbide since all the specimens were placed in the interior of the muffles where conditions were oxidizing at nearly all times. The completeness of decomposition of the silicon carbide was, as would be expected, proportional to the temperature to which it was exposed. The great swelling and disintegration of the cylinders at such low temperatures as 800°C or less was rather surprising. This in turn can be traced to the oxidation of silicon carbide to cristobalite, the presence of the latter being quite definite. In the high temperature specimens, however, much of the cristobalite was volatilized and carried away, but in the low temperature cylinders this was not possible. In the latter, therefore, the cristobalite accumulated, producing an increase in the original volume of the cylinders. This produced the disintegration and dusting, since the temperature was too low for sintering to take place. At intermediate and higher temperatures there was apparently sufficient vitrification with the formation of cristobalite on the outer surfaces as a protective coating to prevent much further oxidation and swelling. In some instances where cracks did form, oxidation and volatilization apparently penetrated along these

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cracks, eating out the interior until only the outer shell of cristobalite remained.

In summary then, silicon carbide under oxidizing conditions seems to be sensitive to low as well as to high temperatures. Thus, long exposure in an oxidizing atmosphere at low or intermediate temperatures breaks it down more or less completely to cristobalite with consequent swelling and disintegration. It must be remembered, however, that the time factor here is large.

Spark Plug Bodies

It was natural of course that those carrying out these experiments should desire to know what might happen to a spark plug body upon exposure to different temperatures for such a long interval. To determine this, numerous spark plugs which had already received the usual firing were placed along the kiln. Some were placed in the interior of the silicon-carbide muffles but the majority were distributed among the port holes of the muffles from the cold zone to the hot zone. A few were placed along the forward part of the cooling end of the kiln but showed no changes. Petrographic examinations were made of all.

Behavior of the Glaze

In all specimens the glaze had been progressively absorbed into the body as the temperature increased. At the higher temperatures it is quite possible also that some of the glaze was volatilized. In either case as the glaze disappeared there was a crystalline growth of needle-like crystals of mullite. As a result of this the ware took on a dull appearance. These crystals of mullite are practically always present microscopically in even the clearest glaze of any porcelain body, especially at the junction of the body and glaze. The unusual growth of crystals here appears to be the result of favorable conditions of time and temperature and concentration of the crystalline portion of the glaze by the removal of the excess glassy matrix. Thus the bodies appear to have a crystalline glaze.

Effect on Crystalline Development in the Body

The average once-fired body shows a high percentage of minute, roughly rectangular crystals of mullite with square cross sections, embedded in a glassy matrix (Fig. 6). These are generally about twice as long as they are wide and in actual size measure about 0.0001 to 0.0002 in length by 0.00005 to 0.0001 inch in width.

At temperatures of 1200°C and lower there seems to have been little effect on the body in increasing the size of the original crystals. At no time did they become essentially larger or show a better development than the average once-fired body. At 1296°C, however, there was a distinct increase in the size of the crystals and a definite sharply angular development. At this temperature they averaged twice the size of those of the usual once-fired body. At a temperature of 1462°C their average size was from four to five times as great and the sharpness of crystal outline was also very marked.

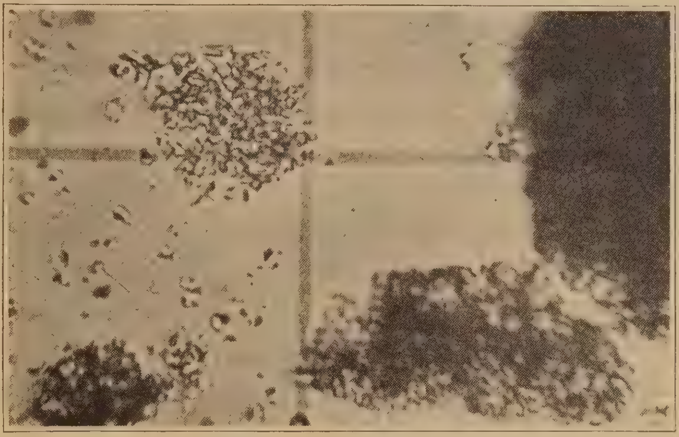

Fig. 6. Photomicrograph of fragments showing the development of mullite crystals in a regular one-burn spark plug body. Magnification 525 times.

One group of bodies is especially worthy of mention because they were placed just in front of the rear burner of the hot zone. It is impossible to state the temperature except that it must have been far above 1462°C, the temperature of the kiln in the hot zone. Both the surfaces and cross-sections of the bodies showed a distinctly crystalline nature and in some places needle-like crystals up to $\frac{1}{16}$ to $\frac{3}{32}$ inch in length were observed. These bodies showed a very white color on the tips and had become distinctly translucent. This was due, as microscopic examination showed, to the unusually large crystals developed (Fig. 7). Microscopically, the mullite crystals were unusually large and perfectly formed. It was difficult to find a fragment showing the complete length of a large crystal but crystals with cross-sections of 0.0015 inch were common. Judging from the size of the cross-section, the length of such crystals might easily reach 0.01 to 0.03 inch. In view of this, the translucency of these plugs is easy of explanation because the innumerable small crystals of the originally rather opaque body have coalesced to form a comparatively few large crystals with resultant loss in light-scattering power.

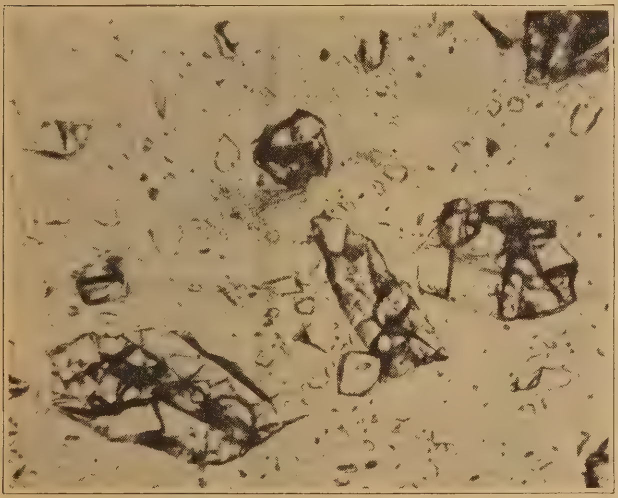

Fig. 7. The same body as in Fig. 6 from in front of the forward burners. Temperature 1462°C+. Magnification 150 times.

Thus, this spark plug body appears to be remarkably resistant, up to 1200°, to further increase in the size of crystals developed and although they do enlarge above this temperature, the increase is relatively small when the time through which they were exposed to these temperatures is considered.

It should also be noted that at no temperature did any of the bodies show the least indication of deformation. Those exposed to the highest temperature directly in front of the burners were mounted vertically. The bases of these plugs stood on silicon carbide. This had gradually volatilized with the result that the bases of the plugs were dark colored probably due to the absorption of carbon or silicon carbide itself.

Absence of Corundum

It is a fact worthy of mention here that even at the highest temperatures to which these bodies were exposed there was no essential change in the crystalline constituents. At no point did corundum appear. The highest temperature even though not known definitely (simply above 1462°C) was well below the temperature (1810°C) designated by Bowen and Greig[1] at which corundum forms in pure Al_2O_3-SiO_2 mixtures but the presence of fluxes such as are present in these bodies might easily have lowered the temperature for the formation of corundum, similarly as it may be found near the walls of soda-lime glass tanks.

Pyrometer Tubes

The pyrometer protection tube specimens were sections of tubes and represent two or three manufacturers' products as well as some vitreous mullite tubes fired at cone 32. The photographs show considerable differences in the quality. Unfortunately these tubes could not be suspended and hence were more or less affected by the refractories on which they were placed as well as fluxes deposited from dust drawn in with the gas and air. However, portions were free enough from contamination to allow much valuable information to be obtained from a study of them. It is evident that gas tightness and long life are largely affected by the silica-alumina ratio and character and amount of fluxes present.

In many instances the pyrometer tubes occupied the same positions as the spark plug bodies and silicon-carbide cylinders. Most of these bodies were unglazed and hence could not be compared to the spark plug bodies in that respect. One body had crazed badly and was very brittle at intermediate temperatures. It was a general observation in this range of temperature that long continued heating tended to make most of the tubes more brittle than they were originally, some more noticeably so than others. The fractures also varied; some were smooth, others rough and pimply.

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[1] *Jour. Amer. Ceram. Soc.*, **7**, [4], 238-54 (1924).

Tubes exposed to temperatures of about 838°C and less showed no change in micro-structure from the original tubes. The constitution of the original tubes is in general quite similar to that of spark plug bodies, namely, numerous small crystals of mullite in a glassy matrix.

One set of tubes exposed to a temperature which was probably about 1050°C was accompanied by a number of widely differing Orton cones. Of these cone 4 was flat. From this we would infer either that there was a sudden increase in temperature at some time or else that owing to the time element involved the cone had fused at a temperature about 150°C or more below its theoretical point. Of the two the latter seems more likely.

These tubes with one exception showed a smooth fracture. There was one noticeable exception to this, which showed a rough fraction and was very brittle. The same resistance toward change in crystalline development was apparent here as in the spark plug bodies. There was no marked change in the size of the crystals, their development being only a trifle sharper (Fig. 8).

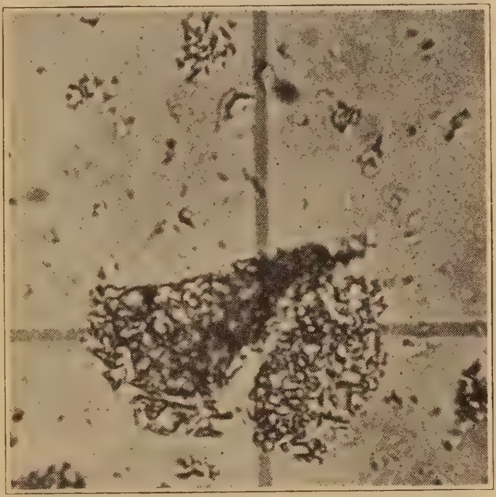

Fig. 8. Photomicrograph of a pyrometer tube body showing the size of the mullite crystals. Temperature about 1050°C. Magnification 525 times.

Another set of tubes exposed to a temperature of about 1200°C showed cone 13 fused. Here again the actual temperature was well below that of the indicated cone temperature. Some of these bodies had a smooth fracture, others were rough and brittle. On some of the latter the fracture surfaces showed numerous white, pimply areas and the whole body was badly crazed. The size of the crystals in these bodies was not noticeably greater than in a once-fired body (Fig. 9). It does not seem possible therefore that the brittleness, roughness of fracture, and crazing can be due to any unusual crystal growth, since the crystals did not vary from those of satisfactory bodies. It seems probable that these qualities are connected with the chemical composition of the body and possibly also may be due to gases present and the state of oxidation or reduction of the kiln.

At a temperature of 1446°C+ with cone 30 flat and cone 32 slightly tipped, all bodies with the exception of the one once mentioned previously showed a smooth vitreous fracture. The exception, although smooth in fracture, was badly blistered and full of holes. As might be expected, these bodies distinctly showed the effect of the high temperature. The mullite crystals averaged from four to six times the size of those of a once-fired body (Fig. 10). In the blistered body the crystals were especially large and perfectly developed and glass was quite abundant. This might be taken to indicate the presence of more flux than in the other bodies, which in turn might easily lead to blistering.

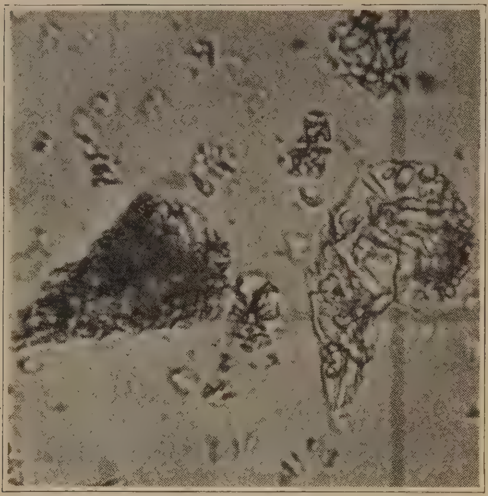

FIG. 9. Pyrometer tube body at about 1200°C. Note that the mullite crystals are only slightly larger at this temperature. Magnification 525 times.

Finally, a group of bodies just in front of the rear burner where the temperature was far above 1462°C was very crystalline in nature. Crystals as large as 0.08 inch were visible. All the bodies had a smooth crystalline fracture and were fairly tough. All showed distinct flattening from the effect of flow under the extreme heat to which they were subjected. As in the case of the spark plug bodies from the same position, the crystals of mullite were very large (Figs. 11 and 12). Rounded ends were quite noticeable, possibly indicating a temperature near that at which they might break down into corundum and

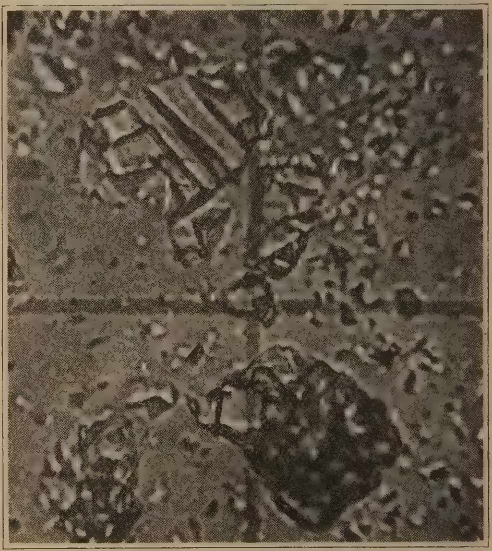

FIG. 10. Pyrometer tube body at about 1446°C. The crystals have grown much larger but not as large as might be expected. Magnification 525 times.

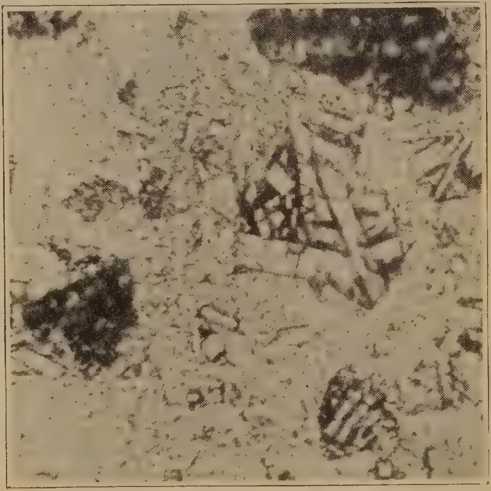

FIG. 11. Pyrometer tube body from in front of the forward burners. Temperature 1462° C+. Note the increased size of the crystals at a magnification of 150 times, slightly more than $\frac{1}{4}$ that of Fig. 10.

liquid. No corundum could be observed, however. The whole group of bodies showed the effect of the greater heat. The greater toughness of this group seems to indicate that the increased temperature has had a beneficial annealing or similar effect as compared to those at 1200°C.

These pyrometer tube bodies can only be roughly compared to the spark plug bodies. Both physically and microscopically most of the compositions appear to be less refractory than the spark plug bodies. Neither do the latter show the blistering, crazing, or rough fracture effect of the pyrometer tubes, and thus are more stable.

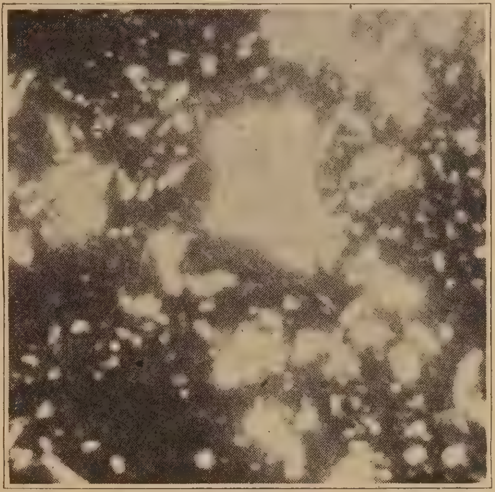

Fig. 12. Same field as Fig. 11 taken between crossed nicols. The bright, strong double refraction shown by the crystals gives some idea of their size and thickness.

Silica Brick

While other samples were being taken it was thought advisable to make brief note of the changes which had taken place in silica brick from the hot zone. For this purpose three samples were taken which served to give both a horizontal and vertical cross-section of the zone. The three samples showed well the variation in temperature through the hot zone.

The first sample was from the bench at the beginning of the zone. Externally it was white but beneath the surface it showed an appearance rather like that of a stock brick. The temperature at this point was approximately 1300°C. Microscopically it showed a low quartz and fairly high tridymite content with much cristobalite exhibiting no definite crystallization. The amount of quartz was not over 10% and probably was much higher in the original brick with correspondingly less cristobalite and tridymite. The facts that tridymite does not predominate now, that the crystals are not especially well developed, and that the quartz is very low, would seem to indicate that the temperature was usually above the tridymite-cristobalite inversion point. This does not necessarily mean that the temperature was above 1470°C, because the small amount of flux present in the brick might lower the inversion point noticeably.

The other two bricks were taken from the hottest part of the kiln, one from the bench and the other directly above, from the center of the crown. They show in their microstructure not only that the temperature was higher than the point where the first brick was located but also that the temperature varied vertically as well. The brick from the crown showed much larger crystals of cristobalite and also a much more vitreous character than that from the bench below, indicating directly a definitely higher temperature. The presence of no other form of silica than cristobalite except a very few tridymite crystals shows that the temperature of both bricks was practically continuously above the cristobalite-tridymite inversion point.

The brick from the crown was very porous and vitreous in character and the mortar had disappeared to a considerable extent. This leads to the possibility that some of the fluffy silica glass found in the cooler portions of the kiln may have been due in part to the volatilization from the silica crown.

Owing to the fact that the crown was not dismantled it was impossible to trace the effect of the heat upon the brick from the inner to the outer side of the crown.

Bonding Materials

A number of bonding materials were tried out through the hot zone. Generally they were used to cement 2-inch cubes of other material, which were placed in the lower port-holes of the silicon-carbide chambers. Three general types of bonds were used, siliceous, fire-clay, and chromium. All were subjected to temperatures of about 1460°C.

The siliceous bonds generally had formed cristobalite with a little tridymite. Usually some glass and mullite crystals were present probably having been derived from a small amount of clay binder.

The fire-clay bonds had generally formed considerable amounts of glass in which were numerous crystals of mullite. In several instances the glass had been absorbed into the brick or had flowed away leaving very little bonding material. In some instances almost the only remaining product was needle-like crystals of mullite sometimes reaching $\frac{1}{8}$ inch in length. These were usually covered with a thin coating of glass.

The chromium bond also had decomposed to form a glass containing mullite crystals and in most cases had flowed away from the joints. It was rather surprising upon breaking apart two of the bricks to find some grayish metallic matter with yellow and blue tarnish colors. This was not analyzed but one would suspect that some chromium had been reduced.

Of the three types of bonds, those of highly siliceous nature stood up best. They had swelled slightly, as could be seen from the manner in which the bond bulged out beyond the surface of the brick at the joint, due to the formation of tridymite and cristobalite. Although resistant to fusion they had but little bonding power and could be expected to do nothing more than fill the joint.

The fire-clay and chromium bonds formed too much glass to prove satisfactory at these temperatures.

Mortar for Silicon Carbide

It may be of interest to call attention here to the behavior of the mortar used in setting the silicon-carbide chambers. This was composed of silicon carbide and clay. When the kiln was finally opened it was found that the mortar had swelled very noticeably and as a result had squeezed out from the joints. The net result was to form an exceedingly tight joint between the chambers. The cause of this might be due in part to the natural expansion of the chambers but undoubtedly the major cause was that revealed upon microscopic examination.

This examination showed a very large amount of granular cristobalite with silicon carbide, mullite, and some glass. The cristobalite had apparently formed from the oxidation of the silicon carbide and because of the siliceous character of the product it had been able to counteract any tendency of the fluxing action of the glass formed from the decomposition of the clay. Thus, not only was a very refractory bond formed but also one which made very tight joints. It was rather fragile and did not have much bonding power, its value being in the other directions mentioned.

Incidental Products Noted

Silica Glass It is a curious fact that this was noted in several places along the cooler portions of the kiln but not in the hotter zones. It took on two distinct forms. One was in the form of a white coating, extremely light and fluffy in character, with a smooth outer surface resembling that of a mushroom. It coated the clay chambers and also the ports of the chambers to varying thicknesses which sometimes reached a depth of one inch. It was especially thick and abundant along the upper edges of the chambers and the higher portholes (Fig. 13). A partial analysis showed variations from 97.32 to 98.42% SiO_2, the remainder being largely Al_2O_3 and Fe_2O_3.

A second type was fibrous in character and was built up and bent around corners in such a manner as to indicate the direction of the convection currents of the kiln gases. It seemed to be confined entirely to the lower port-holes in the clay chambers and was not nearly as extensive in range or amount as the first type.

The way in which these deposits of silica were distributed through the kiln presented rather interesting questions. First, the distribution of the deposits along the walls was not even. While one side of the kiln might show considerable amounts of the deposit, the opposite wall might be free or nearly free from it. Also, where it might be present largely on the upper edge on one side, the reverse might be true on the opposite side. The smooth-surfaced type might be opposite to the twisted, fibrous type. Furthermore, there were considerable breaks in the distribution of the deposits along the kiln. Areas of abundant deposits would cease abruptly only to reappear again farther on toward the hot zone. Why these phenomena should occur with such irregularities is rather puzzling and it may suggest that we do not know quite as much concerning the kiln gases and their circulation as we think, and that we still have something to learn concerning this.

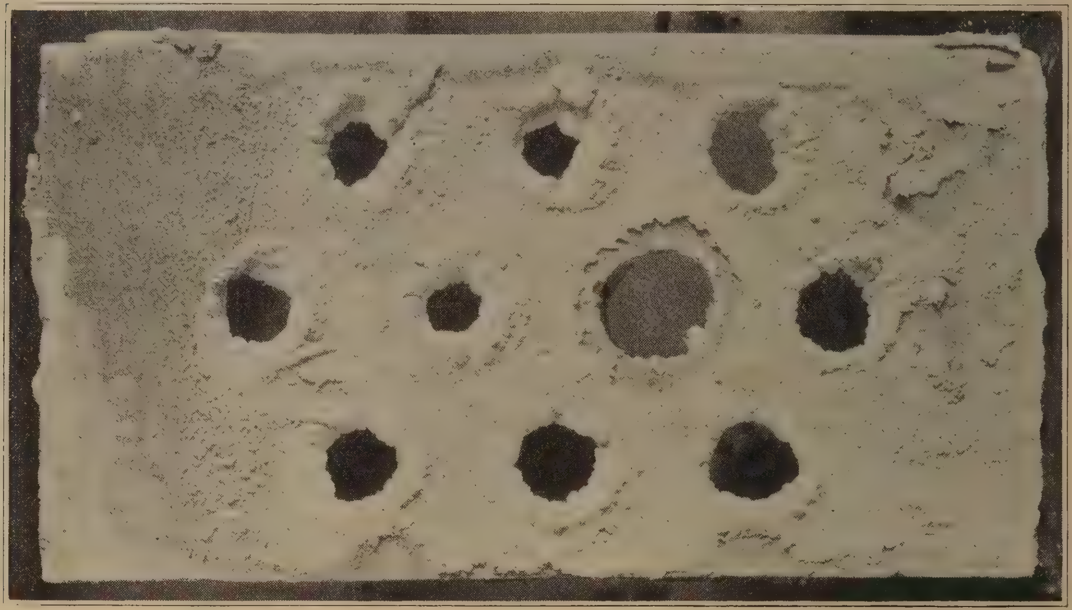

FIG. 13. Mushroom-like deposits of silica glass formed in the water-smoking zone. One port hole has been cleared away to show how the material nearly filled the openings.

The source of this deposit of silica is another interesting question. There appear to be two or three possible sources. The first is that under the influence of water-smoking of the ware some silica was volatilized. This does not appear likely owing to the comparatively low temperatures involved. Yet one must remember that highly heated water vapor has a very pronounced solvent power, but this is more particularly true under conditions of high pressure not present in this case. A second possible source is the silica brick crown of the hot zone from which silica may have been volatilized and carried to the cooler portions of the kiln for deposition. The silica brick were somewhat porous where exposed in the crown but sufficient volatilization does not appear to have taken place to warrant it having been the source of all the silica deposit. The third possible source is the silicon-carbide muffles of the hot zone. These had been oxidized to varying degrees especially in the vicinity of the forward burners. The temperatures here were, of course, very high and in an oxidizing atmosphere silicon carbide decomposes, one of the products being gaseous SiO_2. Thus, if SiO_2 gas from the hot zone was carried to the water-smoking area, ideal conditions would be present for the powerfully oxidizing water vapor to complete the oxidation to SiO_2 and also suddenly cool the SiO_2 vapors with consequent deposition of silica glass. If conditions in the hot zone were only intermittently oxidizing, deposition would also be intermittent.

Incidentally similar light, fluffy deposits may be observed in the hood of an arc light where the silica has been volatilized from the clay binder of the carbons in the presence of air and deposited on the cool hood.

Magnetite (Fe_3O_4)-Hematite (Fe_2O_3) Deposits

These were found at the beginning of the cooling zone, coating the lining of the intake of the damper box as well as various test specimens which had been placed there. They sometimes formed a thin coating of minute, black, glistening, closely crowded crystals while at other points they projected from the surfaces of objects in branching arborescent forms (Fig. 14). In a few cases where they had formed on glazed objects, such as spark plugs, fusion with the glaze had taken place and a black discoloration resulted.

The crystals were formed at atmospheric pressure or greater and under fully oxidizing conditions, since the air used for cooling the ware was fresh air which was drawn from the outside at the exit end and forced into the kiln toward the hot zone.

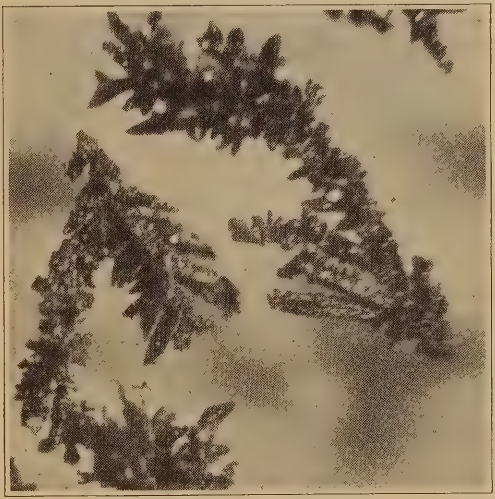

Fig. 14. Some isolated groups of arborescent magnetite-hematite deposits. Magnification 40 times.

Some of the masses of crystals showed magnetism while others failed to show it. Microscopic examination showed the crystals to be composed of both hematite and magnetite.

Hostetter and Sosman[1] have shown that Fe_2O_3 dissociates with measurable pressures at 1100°C into Fe_3O_4 and free oxygen, and that the dissociation undoubtedly begins at a lower temperature, perhaps

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[1] *Jour. Amer. Chem. Soc.*, **38,** 1188-98 (1916).

1000°C, and increases with higher temperatures. The presence of hematite (Fe_2O_3) therefore would indicate a temperature of formation of less than 1000°C. But in this case the form of the crystals indicated that of the octahedron, for although exact measurements of the crystals were precluded owing to their poor development, a low magnification showed them to be eight-faced, with the long axis a tetragonal axis. This corresponds to the form in which magnetite commonly crystallizes whereas hematite crystallizes in hexagonal forms. It is apparent then that the crystals originally formed as magnetite (Fe_3O_4) and as such should have formed at a temperature above 1000°C. Thus, it would appear that the temperature of the kiln in this vicinity never dropped below 1000°C for any considerable period of time. How much higher the temperature might have been, cannot be told accurately but a series of cones from 13 to 26 placed in the intake and upon which crystals had formed, showed no indications of fusion. The limits of the temperature then would be below a theoretical 1390°C and, according to Hostetter and Sosman, above 1000°C, in all probability very much closer to 1000°C. However, thermocouple No. 12 in the crown nearly opposite the intake registered a temperature of near 840°C. This points to the conclusion that under the condition of prolonged heating as was present in this case, the temperature of dissociation is very probably much lower than indicated by the work of Hostetter and Sosman, perhaps as low at 850°C.

According to Sosman,[1] the dissociation temperature of Fe_2O_3 at atmospheric pressure cannot be lowered unless solid solution of Fe_3O_4 in Fe_2O_3 takes place, a point not yet definitely proved. Since the facts of the present instance point toward the dissociation temperature being lower than previously supposed, the possibilities of solid solution having taken place are somewhat more certain than formerly indicated. We are not prepared at present to make a definite statement in regard to this but we hope to have analyses of crystals from different points in the kiln available in the near future, which will show whether there is any variation in the FeO content.

The presence of Fe_2O_3 in these crystals can be accounted for by the fact that as the kiln cooled below the dissociation point, oxygen was absorbed from the air by the Fe_3O_4 until Fe_2O_3 resulted. Thus there was formed what is known in mineralogical terms as a pseudomorph (false form) of hematite after magnetite, the crystal form being that of the magnetite originally formed while the chemical composition is more or less that of hematite.

The source of the iron which formed these crystals would seem to be derived from the wheels and frame of the cars carrying the ware and in part also from the water-cooling pipes along the floor of the kiln in this zone. The fresh air introduced to cool the ware might easily oxidize the hot iron parts of the car and carry the resulting iron oxide vapors along to be deposited in the damper boxes. Any moisture in the air would increase the oxidation markedly.

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[1] Private communication.

Cristobalite Lithophysae On many of the silicon carbide specimens which were in front of the forward burner of the hot zone, white, shell-like, crater formations up to an inch in diameter were observed (Figs. 5 and 15). These bear a very striking similarity to the cavities known as lithophysae (stone bubbles), found in certain types of igneous rocks. The craters formed on the silicon carbide usually possessed only a single rim and because of this were not quite so perfectly developed as those found in rocks. Natural lithophysae are usually made up of a series of concentric rings or rims of rock so that the result is in appearance similar to that of a flower with its concentric layers of petals. The cristobalite lithophysae, although mainly showing only a single shell, do show by the presence of fine horizontal grooves on the outer side of the craters that they have been built up discontinuously.

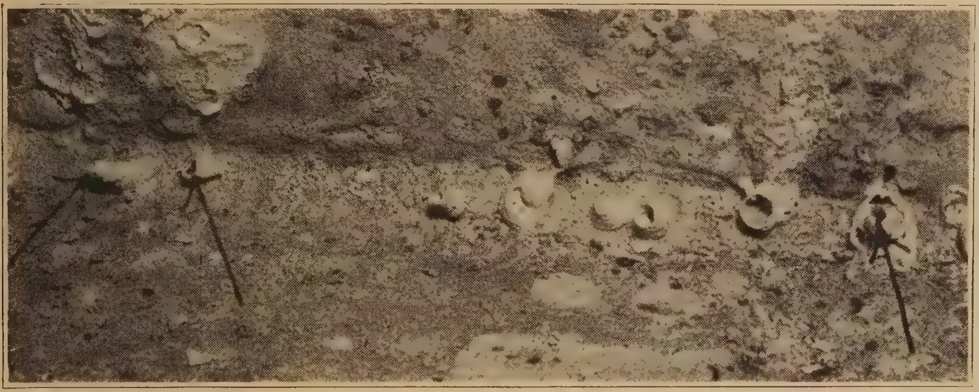

FIG. 15. A close view of a row of lithophysae formed along a joint in the silicon-carbide muffles. See also Fig. 5.

As has already been indicated these craters were built up of cristobalite which could be seen microscopically to be composed of irregular grains or cubical or skeletal crystals. Outwardly, the craters are pure white in color, quite smooth, and vitreous.

The lithophysae in rocks are supposed to result from dissolved gases in the molten rock magma breaking through the viscous mass which immediately afterward solidified. The phenomenon may closely resemble that which takes place when a thick pudding boils except that the cavity does not close after the escape of the gas. Possibly, also, the lithophysae in rocks have been formed by the deposition of material from circulating gases in the cooling mass. The craters formed on the silicon carbide were probably built up by the deposition of material at irregular intervals. No doubt the intense heat from the burners decomposed the silicon carbide and SiO or SiO_2 gas formed. As the gas escaped from the body and came into contact with the oxidizing atmosphere at the surface, SiO_2 would be formed and deposited as cristobalite. The chambers being under a minus pressure also drew some gases through small leaks in the joints of the chambers and built up craters of cristobalite at those points. If conditions varied to other than oxidizing, deposition would stop and with a change again to an oxidizing atmosphere it might be resumed with upbuilding of the crater. Thus, we can account for the irregularity of deposition as shown by the horizontal rings on the shells.

Summary

Under oxidizing conditions where the time factor is great, silicon carbide appears to be sensitive to temperatures as low as 600°C, as well as at extremely high temperatures. At the lower temperatures, oxidation to cristobalite is accompanied by great expansion. At high temperatures, expansion is not so pronounced but volatilization is very great.

The spark plug bodies used, proved to be very resistant to changes in microstructure up to 1200°C. The increase in the size of the mullite crystals above this temperature is relatively small, temperatures considered. No corundum was developed in the bodies at even the highest temperature to which they were exposed nor were any signs of deformation apparent, although at high temperatures the glaze had usually been absorbed or volatilized.

Pyrometer tubes showed the same crystalline components as spark plug bodies but not the same resistance toward increased size of crystals with temperature. The refractoriness was less and the tendency toward blistering and crazing was greater in the pyrometer tubes.

Silica brick from the hot zone showed variations in microstructure (both horizontally and vertically) in accord with temperature conditions prevailing.

Siliceous bonding materials stood up far better than fire-clay or chromium bonds. A silicon-carbide mortar used for the silicon-carbide chambers in the hot zone showed oxidation to cristobalite with consequent swelling which resulted in a very tight joint.

Three incidentally formed artificial minerals were found. Silica glass, occurring in the water-smoking zone, was probably derived from volatilization of silicon carbide and silica brick in the hot zone with precipitation of silica glass when the SiO_2 gases came in contact with the steam in the water-smoking area. Crystals composed of a mixture of Fe_3O_4 and Fe_2O_3 were found in the cooling zone under conditions of temperature, pressure, and oxidation that point to a possibility of the dissociation temperature of Fe_2O_3 being lower than previously supposed. On many specimens of silicon carbide within the muffles of the hot zone lithophysae composed of cristobalite had been formed through oxidation of silicon carbide.

Discussion

C. F. GEIGER: The combustion chambers used in the Dressler tunnel kiln in which these tests were run were commercially manufactured silicon-carbide refractories and the photographs show no evidence of any such oxidation of these chambers as Dr. Peck found with his laboratory test samples of bonded silicon carbide grain.

We believe that these combustion chambers are considered quite satisfactory for this kiln and it must be admitted that there necessarily is a vast difference in quality between Dr. Peck's test samples and these chambers which have been in service a longer period than the eighteen months during which they were exposed to exactly the same conditions as the samples.

A. B. PECK: Everybody realizes that under oxidizing conditions you cannot expect that material to stand up. I do not think ordinarily we expected it to stand up, but, it is rather interesting from the scientific standpoint that you had that oxidation at the extremely low temperature.

T. CHRISTIAN: I have had a little experience with silicon carbide and the results almost parallel these conditions, but, the time factor is very different. I made up some silicon-carbide crucibles, some with clay and some with organic bond. I then placed them in a furnace and held them to about cone 34 for an hour. The results were very similar to the silicon-carbide cylinders spoken of in the high heat zone.

C. F. GEIGER: It is quite evident that the samples Dr. Peck and Mr. Christian have used are not at all representative of silicon-carbide refractories found on the market, and that they certainly are not properly bonded and fired or else they would not have oxidized in the manner or to the degree that they did.

There are many factors governing the development of silicon-carbide refractories and if grit sizes, nature of bond, and a number of other variables are not properly controlled it is very easy to produce a silicon-carbide refractory much inferior to even a poor fire-clay brick.

All varieties of silicon-carbide refractories are not equally good or equally bad. This is the case also with other specialized refractories.

Merely because we start with a valuable refractory material, whether it be silicon carbide, electrically fused alumina, or periclase, for example, it does not necessarily follow that all attempts to bond and fire any of these materials will result in a highly satisfactory finished product, for there is much to be learned about the manufacture of any of these.

Mr. Hudson stated[1] in his discussion of the paper by M. L. Hartmann and O. B. Westmont that he had found that electrically fused alumina refractories were only 12 to 15% poorer heat conductors than silicon-carbide refractories. Mr. Westmont replied that he found that the heat conductivity ratios were more nearly 4 to 1 in favor of silicon-carbide refractories. I am quite sure that these two men did not use the same kind of silicon-carbide brick in their comparative tests. This again shows that very widely different results can be obtained from bonded refractories which are substantially alike in their chief ingredients.

ROBERT TWELLS, JR.: I do not wish to apologize for these specimens because we were working with a different aim in view than Mr. Geiger has in mind. We are not trying to make chambers for the kilns. We are trying to develop high grade silicon-carbide saggers that could be used in our plants and we are experimenting with mixtures, or rather the conditions under which these mixtures oxidize. We are trying to find out whether or not the denser mixtures oxidize more easily, and things of that nature, although most of those things we could determine theoretically. The fact remains that saggers made from some of these mixtures have met our service conditions much better than other mixes which might appear to some observers to be superior.

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[1] *Jour. Amer. Ceram. Soc.*, **8**, [5], 286 (1925).

SOME FACTORS INVOLVED IN THE PREHEATING OF GLASS POTS WITH SPECIAL REFERENCE TO MOISTURE CONTROL[1]

By W. W. Oakley

ABSTRACT

The moisture content of the atmosphere of a pot arch preheating covered pots is a very important factor. Heating in a humid atmosphere tends to equalize the rate of removal of moisture from the inside and the outside surface of the pot at temperatures above 212°, decreasing mechanical strains set up in this process.

Owing to the severity of service on glass melting pots, failure often occurs for no evident reason. Much has been written on the importance of the preheating process as to its effect on pot life and many designs of pot arches have been proposed tending to equalize the rate of preheating at all parts of the pot, but these proposed designs have seldom been built, owing to construction difficulties and costs. Owing to the fact that good results could be obtained with rather crude types of arches under properly adjusted conditions, it has become more or less prevalent to entrust the preheating of the pots to one man who has developed his own methods for the delivery of a hot pot without any visible checks to the pot-setting gang. Furthermore, if checks were not visible, the only test for the soundness of the pot was to tap it with a rod to see if it would "ring" true.

This paper is written with the idea of calling attention to some of the difficulties involved in the technical control of the operations involved in preheating pots with the hope that it may help the glass manufacturer in clearing up some things difficult to understand. There are three considerations involved in preheating pots: (1) requirements, (2) the apparatus used, (3) methods. A pot may vary in thickness from possibly six inches at the bottom to as little as two inches at the crown. It may weigh 3000 lbs. It is delivered to the preheating arch which may be at a temperature of anywhere below 130°F. This temperature may not be a desirable condition but it is often a fact. The pot is a covered, hollow object, dried on the outside faster than on the inside, as the inside humidity while drying will be at least 10% more than the outside, regardless of all efforts to equalize it. Under these conditions the outside is certain to dry faster, resulting in a side wall strain.

When the pot is arched it will contain at least 1½% mechanically retained moisture. The combined moisture will vary with the composition. In addition to the drying strains, the pot may have strains set up by rough handling.

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[1] Received in revised form October 28, 1925.

There are four fuels which are used for heating arches:

(1) **Coal** The use of coal is attended with a great probability of temperature fluctuations due to firing methods and especially fire cleaning. Much of this variation can be minimized by constructing the arch with more than one firebox, which, however, entails further expense and, likewise, is often somewhat difficult to accomplish where small arches are badly crowded. Furthermore, the purchase of coal with existing markets results in a tendency on the part of the management to change grades, and this in turn tends to perplex the firemen.

(2) **Natural Gas** This is the ideal fuel for this purpose. It is to be remembered, however, that unless comparatively large piping is used and a good pressure maintained the adjustment on one arch may affect the adjustment on another.

(3) **Oil** Oil is subject to difficulty with the burners at low temperatures. This makes it difficult to secure a uniformly rising temperature. Furthermore, with arches built more or less in the open, trouble is experienced with frozen air lines and sluggish oil in cold weather. Also, at high temperatures it is especially severe on the firebox.

(4) **Producer Gas** When used in the raw, hot condition it is difficult to secure a satisfactory temperature gradient using this fuel at low temperatures, owing to the size of the valves necessary for eliminating soot trouble. The gas supply is subject to firing conditions and the building up of troublesome soot deposits. Furthermore, the cost of equipment is expensive and considerable space is required. Where there are more than two arches the adjustments of one will seriously affect the adjustments on the other, so that the use of this fuel requires considerable attention.

The empiric practice developed for preheating pots differs decidedly from that used in firing solid clay objects such as tank blocks. The problem of firing blocks is one of driving out the moisture at a rate slow enough to avoid checking and then removing this moisture from the arch or kiln as rapidly as possible by admitting sufficient air to pick it up and carry it up the stack. The admission of this air tends to even up temperature conditions so that the use of a draft gage and a good temperature measuring installation will closely indicate the uniformity of firing results. Furthermore, checks in a tank block do not necessarily affect the life of the tank, whereas checks in a pot cause premature failure.

In heating a closed pot in an arch the inside surface of the pot is heated almost entirely by conduction from the outside. Unless care is used, the portion of the pot nearest the firebox will be heated much faster than either the inside surface or the outside surface farthest from the firebox. The only way to increase the rate of heating on the cool side of the arch is to use enough excess air to equalize it. This in turn tends to heat the outside surface much faster than the inside, thereby setting up strains in addition to those produced in drying. It was found out very early apparently that this excess air would cause checks and hence the practice developed by which the flues were kept closed absolutely tight as long as possible. While this heated the pot unevenly, the checks ceased. This practice naturally resulted in a very smoky fire being used at low temperatures and was only justifiable from a fuel viewpoint on account of the results obtained. Air leaks were carefully stopped, regardless of the relative pressure inside and outside the arch. Arches were located where there would be a minimum of wind. The soot covering the pot supposedly protected it and when the temperature could no longer be increased, the damper would be opened. This would immediately cause a complete change in the temperature distribution in the arch.

Furthermore, this practice occasionally caused unexpected results. A damper might break. Two arches on the same stack might affect each other or the amount of air drawn into the arch under these conditions, being dependent on leakage, might vary considerably. To overcome some of these problems, temperature measuring and draft recording apparatus were used and a close control at low temperature demanded. For the first day a temperature increase of 3° C per hour may be scheduled. This, however, involves difficulties. First, with the more or less standard method of handling the arch adjustment, the top of the arch is hot when the bottom is cold. The only method by which anything can be determined as to bottom conditions is by the installation of a bottom element. As arches run at temperatures under which base metal couples will not operate, a platinum couple is required for this service and a couple long enough for bottom control is very expensive. Likewise, its installation is difficult and always subject to serious damage in removing the pot. Pyrometric cones used on the bottom simply indicate the maximum temperature reached. Even though the outside of the pot is of uniform temperature, there still exists the question of lag in temperature on the inside.

In considering the above factors it is quite apparent that even when temperature schedules are worked out correctly and used carefully, the only point in the pot that will be fired according to schedule is that nearest the element. Under these conditions it is entirely possible to add sufficient fuel to keep the element on schedule, the balance of the heat being pulled downward by the draft, causing a rapid increase in temperature of the bottom of the pot. This can be minimized to a certain extent by stopping the temperature increase at the time the damper is opened, allowing the bottom of the pot an interval to heat to a point nearer the top. In spite of this, however, it is apparent that severe, uncontrolled temperature shocks occur even when the elements read correctly.

In view of the work done in emphasizing the value of humidity control in drying, the extension of the same principles in the firing apparatus might be used to minimize the strains set up at the early stages. In considering this question an analysis of the conditions brought out the following fairly consistent facts:

(1) All fuels except possibly anthracite coal contain large amounts of hydrogen which upon burning results in a flue gas containing moisture. In all considerations of flue gases when tests are made by chemical methods, the moisture disappears in the apparatus, causing its effect to be lost sight of. The moisture content of the flue gases from common fuels is shown in Table I.

TABLE I

Fuel	Cu. Ft. Water Vapor per 1000 B.t.u. Liberated.	Percentage Water Vapor by Volume in Flue Gases.
Dry Pittsburgh coal	.0639	4.09
Dry hot producer gas	1.5	10.3
Fuel oil	1.362	12.48
Natural gas	1.92	17.5

It is to be observed that the combustion of natural gas gives the wettest flue gas. Producer gas gives the driest.

(2) Pots do not check as easily when heated with oil as when heated with producer gas.

(3) Men of long experience know that it is easiest to get good pots from the arches during the latter part of summer when the air carries most moisture. This was ascribed to weather conditions, there being less wind at this time.

(4) The deposition of soot on the pots indicates insufficient air. As the moisture content of the air admitted is lower than that which exists in an arch firing a clay object, this soot indicates that a maximum amount of moisture exists in the arch. The experienced operator does his best to maintain this soot.

(5) The sealing of the damper conserves the moisture driven out from the pot, increasing the moisture content of the arch atmosphere.

(6) The experienced operator will go to extreme measures to stop drafts around the back of his arches in the winter when it is dry even though this air cannot possibly get into the firebox except through controlled openings.

(7) In studying temperature conditions large amounts of heavy-

unfired blocks were placed in back of the pots in order to protect them and again good results occurred. These blocks would naturally tend to increase the moisture content.

(8) Pots in the front of arches often appear to be better than those in back.

(9) Finally during 1919 and 1920 owing to production conditions we were compelled to heat up a furnace immediately after a clay siege was built. There was no time available for drying out the siege in spite of the fact that this was the traditional practice. When the temperature reached 100° C, the atmosphere of this furnace was soaking wet. Under these conditions it did not seem at all possible that the pots would survive. No trouble at all was experienced, however, the average pot life being well above that usually obtained. Later a second furnace was handled the same way with the same results.

The facts all indicated that the maintenance of moisture in the atmosphere surrounding a pot while heating up was of maximum importance in minimizing strain and that there was little to fear owing to too much moisture being present.

The problem then was one of methods of controlling the amounts of moisture introduced. An arch may require for combustion during the period in which we are interested about 1760 cubic feet of air per hour. This air under conditions of 20°F and 55% relative humidity contains only 8% as much moisture as at 85°F and 70% relative humidity. To raise the moisture content of the air to summer conditions it is necessary to add only two pounds of water per hour, corresponding to about .24 gallons. Any person who has undertaken the burning of fuel oil in as small quantities as this will appreciate the difficulty of obtaining the necessary control. Furthermore, it is to be noted that in order to hold the moisture content of the ingoing air constant, the amount of moisture added should not only tend continuously to increase as the air demanded for combustion increases with the temperature, but must be varied with temperature and humidity conditions which are constantly changing. These conditions can only be met exactly by using air of constant temperature and humidity which, of course, is out of the question.

The first attempts made consisted of placing orifices in a water line and allowing the water from the orifice to drop in the stream of ingoing gas. This was very troublesome due to stoppage, as such an orifice was about $\frac{1}{32}$ inch in diameter. An orifice was then substituted using high pressure steam. Even this resulted in a very small orifice which was subject to a varying percentage of moisture, the small amount being used causing it to stand in the pipes long enough for severe condensation. Next, water was boiled at a definite rate, allowing the steam to enter the arch. This entailed the addition of a definite volume of water at definite time intervals to a small boiling device.

However, the results obtained from a few trials on one arch indicated that the checking of the pots was less severe. In view of the fact that such a crude device tended to improve conditions, we concluded (1) to install a $\frac{1}{4}$-inch steam jet in the offtake from the gas producer, making the steam connection in parallel with the blower jets, and (2) to make a direct steam connection to the arch. As we already used oil for heating the arch at very low temperatures, this steam connection was installed as a substitute for the atomizing air on the oil burner. The results obtained were very satisfactory. We found that fewer checks occurred and those that did occur were of no importance.

The system was then extended to cover the entire bank of arches and no limitation was placed on the fireman as to the amount of steam he might use at any temperature, his instructions simply being to keep the burners blowing steam at the lower stages of the firing.

While the addition of this steam might be expected to increase the fuel consumption of the arch, we have found that it forces the fuel into the firebox better, which appears to neutralize the expected loss. The use of this steam has prevented the overheating of the fireboxes which was inherent in the method used for control, resulting in a decided decrease in repair charges.

Our experience with pots and similar objects led us to consider the possibilities of firing intricate clay shapes by the same principle. On some very intricate glass feeding machine parts where checks would cause rejection of the part it was our custom to consume ten days in firing, the greatest care being used in the temperature control. We have recently tried muffling these parts with damp clay blocks, and have been able to secure more satisfactory firing and no checks with a firing period of six days. We have found that the supervision required and the experience necessary is far less and the difficulties minimized.

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A DEFORMATION STUDY OF VARIOUS ALUMINOSILICATES AND BOROSILICATES[1]

By Kai-Ching Lu

ABSTRACT

A brief review of the past literature on the thermochemical study of silicates, aluminosilicates and borosilicates was prepared. The present study includes the development of five ternary "deformation eutectics," which had the following compositions and deformation temperatures:

Molecular Formula	Approximate Deformation Temperature in °C.
PbO : 0.254 Al_2O_3 : 1.91 SiO_2	650
ZnO : 0.225 Al_2O_3 : 0.906 SiO_2	1360
PbO : 0.238 B_2O_3 : 0.78 SiO_2	415
Na_2O : 1.29 B_2O_3 : 1.73 SiO_2	570
K_2O : 2.11 B_2O_3 : 2.585 SiO_2	655

Cones were made and deformation was studied in the same manner as used with standard pyrometric cones. All eutectics developed are within the $2\frac{1}{2}$ molecular per cent limit. Combination of eutectics were also made but no further lowering of temperature was noticed. The results were discussed with special stress laid upon the relation between the various eutectics.

I. Introduction

The present investigation was undertaken to develop an enamel of low fusion temperature by a combination of several eutectics. The scope of this study was confined to the development of five ternary eutectics which constitute a part of the enamel composition. The idea is by no means a new one and the work is empirical.

The term "eutectic" or "deformation eutectic" is used throughout this paper to designate the composition which requires the lowest temperature to complete its deformation. A combination of these ternary eutectics was also made in proportions that would make an enamel.

Dealing with so complex a mixture as enamel, and with only a scarce amount of data in hand, the author is not able to declare at this stage any possibility that an enamel could be obtained from eutectic combinations, yet he is willing to unveil such light as he has.

II. Review of Literature

A review of the past literature of similar nature gives some idea of the thermochemical behavior of the chief constituents of enamel.

1. PbO-SiO_2 This system has been studied a good deal but no one paid much interest to the high silica side. Mellor[2] took

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[1] A thesis presented for the degree of Master of Science, Ohio State University, 1925. Recd. Nov. 1, 1925.

[2] J. W. Mellor, A. Latimer and A. D. Holdcroft, *Trans. Ceram. Soc.* (Eng.), **9**, 129 (1909-10).

a series of observations on the melting of angular fragments of lead silicate glasses and found the deformation temperatures of the crystal mixtures, except pure PbO, roughly 200°C below their corresponding melting points. Mostowitsch[1] determined the ranges of formation temperature, melting points and freezing points. Cooper studied the thermal behavior[2] and the optical properties[3] and found a sound agreement. Hilpert studied this with Weiller[4] but he went through the same thing afterwards with Nacken[5] and made corrections. Beck[6] in his study of lead silicate glasses measured the softening temperatures of the PbO-SiO_2 mixtures at which the granular materials had run together sufficiently to permit the passage of electric current. Together with the author's result on deformation study obtained along the line PbO-SiO_2 in the ternary system PbO-Al_2O_3-SiO_2, the above data were shown graphically in Fig. 5 (See p. 40).

2. PbO-Al_2O_3-SiO_2 Eisenlohr[7] made a series of lead aluminosilicates with $1PbO : 0.1Al_2O_3$ constant and SiO_2 varying from 1.5 to 3. The deformation temperature of $PbO : 0.1Al_2O_3 : 1.5 SiO_2$ is the lowest being cone 018-019. But Pictorius[8] declared that Eisenlohr's work is inaccurate and cannot be checked. Beck[9] gave the following data on softening temperature (passability of electric current).

	$PbO \cdot SiO_2$	$PbO \cdot 2SiO_2$	$PbO \cdot 3SiO_2$
With 2.5% Al_2O_3	535°C	600°C	630°C
With 5% Al_2O_3	595°C	660°C	700°C

3. K_2O-SiO_2, K_2O-Al_2O_3-SiO_2 In Morey's[10] study of the system H_2O-K_2SiO_3-SiO_2, he obtained two binary eutectics on the straight line K_2O-SiO_2. The eutectic between K_2SiO_3 and $K_2Si_2O_5$ has a composition $K_2O: 1.3SiO_2$ (775°C) and one between $K_2Si_2O_5$ and SiO_2 has a composition $K_2O : 4SiO_2$ (525°C). Rice,[11] in his deformation study of alkali silicates and alkali aluminosilicates, also gave two binary eutectics on the line K_2O-SiO_2, namely $K_2O : 1.29SiO_2$ (780°C) and $K_2O : 7.43SiO_2$ (880°C) and one ternary eutectic $K_2O : 0.276 Al_2O_3 : 6.978SiO_2$ (870°C).

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[1] W. Mostowitsch, *Metallurgie*, **4**, 647-55 (1910).

[2] H. C. Cooper, L. I. Shaw and N. E. Loomis, *Jour. Amer. Chem. Soc.*, **42**, 461-73.

[3] H. C. Cooper, E. H. Kraus and A. A. Klein, *Jour. Amer. Chem. Soc.*, **47**, 273-85.

[4] S. Hilpert and P. Weiller, *Ber.*, **42**, 2969-77.

[5] S. Hilpert and R. Nacken, *Ber.*, **43**, 2565-73.

[6] Beck, Löwe and Stegmüller, *Arb. kais. Gesundh.*, **33**, 203-49.

[7] H. Eisenlohr, *Sprechsaal*, **43**, 389-92.

[8] H. Pictorious, *Sprechsaal*, **43**, 576-77.

[9] Beck, Löwe and Stegmüller, *loc. cit.*

[10] Morey and Fenner, *Jour. Amer. Chem. Soc.*, **39**, 1173-1229.

[11] B. A. Rice, *Jour. Amer. Ceram. Soc.*, **6**, 525-47 (1923).

4. Na_2-SiO_2, Na_2O-Al_2O_3-SiO_2 Morey and Bowen[1] determined two eutectics in the binary system Na_2SiO_3-SiO_2, namely $Na_2O : 2.2SiO_2$ (847°C) and $Na_2O : 5SiO_2$ (793°C). Rice's[12] study also gave two binary eutectics, $Na_2O : 0.972SiO_2$ (830°C) and $Na_2O : 4.579SiO_2$ (860°C) and a ternary eutectic $Na_2O : 0.185 Al_2O_3 : 4.55SiO_2$ (800°C).

5. ZnO-SiO_2, ZnO-Al_2O_3-SiO_2 Jäger and von Klooster[2] found two silicates, $2ZnOSiO_2$ with a melting point 1509°C and $ZnOSiO_2$ with a melting point 1437°C. Watts developed during his study of Bristol glazes[3] a ternary eutectic with a composition $ZnO : 0.324Al_2O_3 : 0.81SiO_2$ and a deformation temperature around cones 12-13.

6. CaO-Al_2O_3-SiO_2 The work of the Geophysical Laboratory of Washington[4] done on this system is well known and very accurate. Hanna[5] studied the deformation temperature and found that the ternary eutectic of lowest deformation temperature coincides with that of the lowest melting point, namely, $CaO : 0.348 Al_2O_3 : 2.489SiO_2$.

7. MgO-Al_2O_3-SiO_2 The work of the Geophysical Laboratory on this system[6] was also well recognized and of equal importance. Watts[7] obtained a ternary eutectic $MgO : 0.392Al_2O_3 : 2SiO_2$ which fuses at cone 12.

8. BaO-Al_2O_3-SiO_2 According to Watts[8] the most fusible mixture has a composition between (*a*) 35% BaO, 10% Al_2O_3 and 55% SiO_2 and (*b*) 40% BaO, 10% Al_2O_3 and 50% SiO_2, both showing signs of fusion at cone 6. Eskola[9] gave in his study of the line system BaO-SiO_2 four compounds, three binary eutectics and a continuous series of solid solutions between $2BaO3SiO_2$ and $BaO2SiO_2$.

9. PbO-B_2O_3, PbO-B_2O_3-SiO_2 Thompson[10] found a compound $PbO3B_2O_3$ but no thermal study was made. Beck[11] gave the softening temperature data as follows:

	$PbO \cdot SiO_2$	$PbO \cdot 2SiO_2$	$PbO \cdot 3SiO_2$
With 5% $Na_2B_4O_7$	450°C	510°C	650°C
With 5% B_2O_3	460°C	540°C	600°C

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[1] G. W. Morey and N. L. Bowen, *J. Phys. Chem.*, **28,** 1167.

[2] Jäger and von Klooster, *Sprechsaal*, **52,** 257.

[3] A. S. Watts, *Trans. Amer. Ceram. Soc.*, **18,** 632.

[4] Rankin and Wright, *Amer. Jour. Sci.*, **39,** 1-79.

[5] Hanna, *Trans. Amer. Ceram. Soc.*, **17,** 672.

[6] Rankin and Merwin, *Amer. Jour. Sci.*, **45,** 304.

[7] A. S. Watts, *Trans. Amer. Ceram. Soc.*, **19,** 453.

[8] A. S. Watts, *Trans. Amer. Ceram. Soc.*, **19,** 457.

[9] P. Eskola, *Amer. Jour. Sci.*, **4,** 331-75 (1922).

[10] H. V. Thompson, *Trans. Ceram. Soc.* (Eng.), **18,** 510-11.

[11] Beck, Löwe and Stegmüller, *loc. cit.*

10. $CaO-B_2O_3$ According to Guertler[1] there are three compounds, $CaO2B_2O_3$ (1012°C), $CaOB_2O_3$ (1100°C) and $2CaOB_2O_3$ (1225°C) and two eutectics, CaO : $1.5B_2O_3$ (995°C) and CaO : 0.887 B_2O_3 (1070°C).

11. $BaO-B_2O_3$ In this system, Guertler[1] found one eutectic with a composition 1.5BaO : B_2O_3 at 750°C.

12. $K_2O-Na_2O-B_2O_3$ Klooster[2] found the lowest fusion temperature of the mixture of KBO_2 and $NaBO_2$ at about 800°C containing equal parts of each.

13. Na_2SiO_3-$CaSiO_3$-$BaSiO_3$ Wallace[3] developed in the straight line Na_2SiO_3-$CaSiO_3$ two eutectics, 80% Na_2SiO_3, 20% $CaSiO_3$ at 938°C and 30% Na_2SiO_3, 70% $CaSiO_3$ at 1140°C. In the straight line Na_2SiO_3-$BaSiO_3$, there was an unbroken series of crystals, the mixture of the lowest fusion point contains 40% $BaSiO_3$. In the straight line $CaSiO_3$-$BaSiO_3$, Lebedew[4] found an eutectic of the composition 65.5% $CaSiO_3$ and 34.5% $BaSiO_3$ at 1040°C. In Eskola's[5] study on silicates of strontium and barium, he obtained a binary eutectic in the line system $CaOSiO_2$-$BaOSiO_2$ of the composition 27.5% $CaOSiO_2$ and 72.5% $BaOSiO_2$.

14. $CaO-MgO-Al_2O_3-SiO_2$ Besides the systems $CaO-Al_2O_3-SiO_2$ and $MgO-Al_2O_3-SiO_2$ the Geophysical Laboratory also carried out the studies on the systems $CaO-MgO-SiO_2$[6] and $CaO-MgO-Al_2O_3$[7], thus having the entire quarternary system completed.

15. $K_2O-CaO-Al_2O_3-SiO_2$ Hanna[8] obtained from combining eutectics of aluminosilicates a mixture of the composition $0.6K_2O$, 0.4 CaO : $0.739Al_2O_3$: $4.829SiO_2$ with deformation started at cone 3 and completed when cone 3 was three-quarters down.

16. $RO-PbO-Al_2O_3-SiO_2$ Using different oxides for RO in the formula 0.3 RO, 0.7 PbO : 0.1 Al_2O_3 : 2 SiO_2 Eisenlohr[9] obtained a series of deformation temperatures: Na_2O, cone 019; K_2O, cones 016-017; BaO, cones 015-016; CaO, cone 015; and MgO, cone 013-014. Peddle[10] included in his article, "The Development of

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[1] Guertler, *Z. anorg. chem.*, **40,** 337.

[2] H. S. von Klooster, *Z. anorg. Chem.*, **69,** 122.

[3] Wallace, *Z. anorg. Chem.*, **35,** 187.

[4] P. Lebedew, *Z. anorg. Chem.*, **70,** 301.

[5] P. Eskola, *Am. J. Sci.*, **5,** [4] 331-75 (1922).

[6] Ferguson and Merwin, *Am. J. Sci.*, **48,** 109.

[7] Rankin and Merwin, *Jour. Amer. Chem. Soc.*, **38,** 575.

[8] Hanna, *Trans. Amer. Ceram. Soc.*, **17,** 672.

[9] Eisenlohr, *Sprechsaal,* **43,** 389-92.

[10] C. T. Peddle, *J. Soc. Glass Tech.*, **4,** 1-107; **5,** 90.

Various Types of Glasses" both alkali and lead glasses but his study was confined to solubilities and refractive indices and very little was said about thermal changes.

III. Methods of Study

Materials The method of study was to make up cones and observe their deformation behavior when heated. The materials used, except B_2O_3 and SiO_2, were C. P. oxides and carbonates. The SiO_2 was potters' flint ground to pass 150-mesh.

All materials were weighed to an accuracy of 0.01 gram to make up a 100-gram batch.

According to Bleininger and Teetor[1] the B_2O_3-SiO_2 mixtures are typical glasses possessing no definite deformation temperatures and the increase of the ratio of $SiO_2 : B_2O_3$ from 2 : 1 to 2.2 : 1 results in a decided drop in solubility, indicating that some B_2O_3 has been rendered insoluble. With this in mind, a B_2O_3-SiO_2 mixture was prepared by fusing together a blend of ground flint and boric acid, 5% more of the latter than is required to make up the ratio 1 : 1. A chemical analysis of the resulting mass gave 46.85% SiO_2 which corresponds to $0.972B_2O_3 : SiO_2$. This was kept over a desiccator and stored up in an air oven held about 120°C. It was then used in the study of the borosilicate series.

The Cones The batch was ground, passed through a 100-mesh screen and thoroughly blended. For each member at least three cones were made from the batch using dextrin as a binder. For the alkali-borosilicate series, molasses seemed to be a better binder. All cones were made about two-thirds standard size except those undergoing a temperature above 2000°F and these were made about quarter size for use in a smaller furnace. In planting the cones in the plaque, a plastic mixture of dextrin and flint was used between the cone and the clay plaque to prevent reaction between the two.

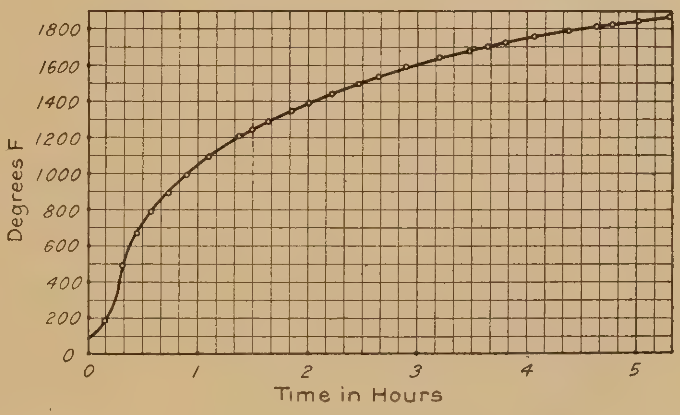

FIG. 1.

The Furnaces The deformation behavior of the cones up to 2000°F was studied in an electrically heated muffle furnace.

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[1] A. V. Bleininger and P. Teetor, *Trans. Amer. Ceram. Soc.*, **14,** 210 (1912).

A Bristol direct reading pyrometer (Fahrenheit) and a base metal thermocouple 25H were used. A typical heating rate curve is shown in Fig. 1.

There were six outside resistances connected to the heating coil. By a rearrangement of the switches, hence changing the total resistance, a slower rate and constancy of temperature could be obtained as desired.

For temperatures above 2000°F a small Meker gas fired muffle was used.

The Data The deformation behavior of the cones was watched from a peep hole in the front door. Comparisons were made with Orton pyrometric cones. Temperature and time were recorded. The deformation was judged by the starting and finishing temperatures and time. With time accurately taken, the interval between "started" and "down" is a measure of the comparative viscosities.

All members on any of the triaxials shown in the following diagrams are given in molecular percentage.

After the member or group of members having a comparatively low deformation temperature was determined the limit of molecular difference between adjacent members was cut and the intermediates investigated. For the "5 and 10% limit" series, the cones were usually made from the raw materials (except B_2O_3) but for the 2.5% limit series, nearly all cones were made from blends of fritted end members. All series were studied to the 2.5% limit. Thus the deformation eutectic (within the 2.5% limit) was developed.

The portion of the cone not imbedded in the plaque was broken off and the rest ground to pass 100-mesh and analyzed. Duplicate analyses were made. The B_2O_3 content was obtained by difference.

IV. Series PbO-Al_2O_3-SiO_2(PAS)

As the PbO was introduced raw, part of it might volatilize during the heating and the clay plaque might absorb some from the bottom of the cone, thus causing a shift in the range of the deformation temperature, but as the percentage limits were not narrow in the first few heatings there is no considerable change in the order of deformation because of loss of lead. The area investigated in this system is shown in the Figs. 2, 3 and 4, indicating the 10, 5 and 2.5% limit respectively.

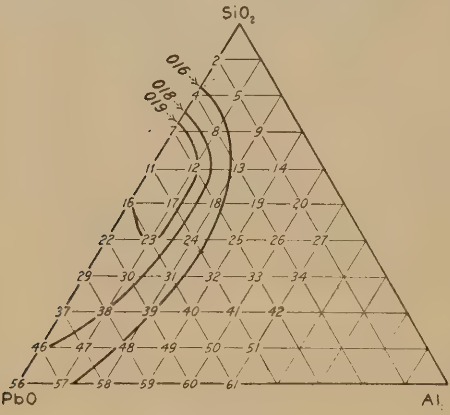

FIG. 2.

TABLE I

FIRST HEATING, SERIES PAS

Triangular area 16-56-61, 10% limit (Fig. 2)

(*a*) Deformation Data

Time	Temp. in F°	Started	Down	Time	Temp. in F°	Started	Down
A.M.							
10:30	on			12:13	1400	47	
10:40	200			12:20			47
10:50	500			12:22			39
11:05	800			12:24	1450	49(broken)	
11:22	1000			12:26		57	
11:30	1080	022		12:30		50(broken)	
11:40	1140		022	12:32		48	
11:50	1280	16		12:34	1500		57
11:55	1285	23		12:40		014, 40	
11:58	1290	30	23	12:43		60(broken)	
11:59		37, 29		12:45		58	014, 40
12:00	1300	22, 38	16, 30	12:48	1550		48
P.M.				12:55		61(broken)	
12:01		46		1:08	1600		58
12:02		018	22	1:10		010	
12:03			29, 46	1:20			010, 49
12:04			37	1:43	1700	06	
12:06	1350		38	1:55		59	
12:09		31	018	2:50	1800		06
12:10		39		3:00	1820 (off)		59 (half down)
12:12			31				

(*b*) Order of Deformation and Time between Started and Down

Starting Order	Down Order	Interval in minutes	Starting Order	Down Order	Interval in Minutes
16	23	3 (following the down order)	46	38	6
			31	31	3
23	30	2	39	47	7
30	16	9	47	39	12
29	22	2	57	57	8
37	29	4	48	48	16
22	46	2	58	58	23
38	37	5	59	—	—

TABLE II

SECOND HEATING, SERIES PAS

Rectangular area 2-11-27-51, 10% limit (Fig. 2)

(*a*) Deformation Data

Time	Temp. in F°	Started	Down	Time	Temp. in F°	Started	Down
12:00 M.	on			1:53			46
12:42	800			1:55	1370		22
12:58	1000			1:58		018	
1:08	1100			2:06	1420		018
1:14	1120	022		2:08			4
1:23			022	2:14		24	
1:25	1200	021		2:16	1450	8	
1:31			021	2:18		13(tipped)	18
1:34		020, 11		2:25		016	
1:35	1270	17		2:30			24
1:36		23		2:31			8
1:37		7	020, 11	2:32	1510	014	016
1:38		019, 12		2:45	1560	012	014
1:39			7, 17	3:15			012
1:40	1300	4		3:17		010	
1:41		37	12	3:20	1670	41(tipped)	
1:42			23	3:32			010
1:45		29		3:40		32	
1:46		38		3:43			32
1:47	1310	16		3:50	1720	08	
1:48		18, 30, 46	29, 37, 38	4:15	1780		08
1:49			019, 16	4:45		51(tipped)	
1:50	1340	22		4:50	1820	06	
1:52			30	5:10	1860(off)		06

(*b*) Order of Deformation and Time between Started and Down.

Starting Order	Down Order	Interval in Minutes	Starting Order	Down Order	Interval in Minutes
11	11	3 (following the down order)	16	30	4
			30	46	5
17	17	4	46	22	5
23	7	2	18	4	28
7	12	3	22	18	30
12	23	6	24	24	16
4	37	7	8	8	15
37	29	3	13	32	3
29	38	2	41	—	
38	16	2	32	—	

In this heating the members along the PbO-SiO_2 side deformed first, the order being 11, 17, 7 and 12. It showed a good check with first heating and only number 23 can be included in this group.

From the results obtained from the last two heatings the area of a low deformation temperature appeared limited to 7-12-16-23. Number 16 deformed together with 29, 37 and 38 but it came down before 22 and 30. Within this area seven intermediate members, *A* to *I* inclusive, were added.

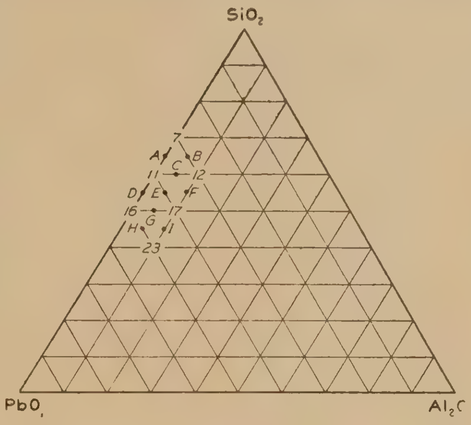

FIG. 3.

TABLE III

THIRD HEATING, SERIES PAS

Rectangular area 7-12-16-23, 5% limit (Fig. 3)

(*a*) Deformation Data

Time P.M.	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
1:30	on			2:55		019	
2:37		022		3:08	1250(off)		019
2:40	1120	021	022	2:47–2:55		all started	
2:44		020	021	3:00–3:08			all except 12
2:51			020				

The interval between start and down of all cones was so short that exact observations were impossible. The temperature taken was approximate. The only record obtained in those eight minutes was the deformation order.

(*b*) The starting order of deformation was not clear, so only the down order is worth recording. At cone 020 *C*, *E*, *G*, *H*, and 23 were down together and the order in which the others came down was 17, 11, 7, *I*, *A*, *B*, *F*, *D*, and 16.

At cone 019, 12 was $\frac{3}{4}$ down.

The area along the 5% Al_2O_3 line including *C*, *E*, *G*, *H*, and 23 seems to be quite near the eutectic composition. They came down at practically the same time and the rest came down after them within eight minutes. This does not necessarily mean that the low deformation mixture must lie on this line. As the cones were made from raw materials, it is quite possible a certain amount of PbO volatilized during the heating.

The heating rate of the fourth series was changed to get a slower temperature increment in order to facilitate the observation of the deformation behavior within small temperature differences. The furnace was raised as usual to about 1000°F and then switched to a slow heating rate, raising the temperature about 20°F per hour.

TABLE IV

FOURTH HEATING, SERIES PAS. (Fig. 3)

Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
P.M.							
1:30	on			3:37½			*C*
3:00	1000			3:38		019	*E*
3:20	1200 (slow rate)			3:40	1200		019
3:26	1200	020		3:50	1210	*H*	
3:30			020	3:52		*G*	
3:34		*C*		3:55		23	
3:36		*E*		4:00	1220(off)		

Within 2.5% limit, eleven members around *C* and *E* were made by blending fritted members *I*, *D*, 7 and 12.

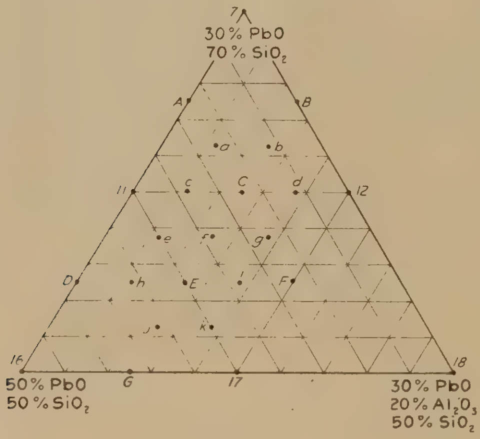

FIG. 4.

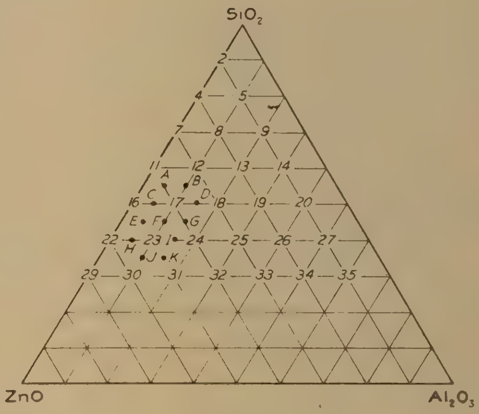

FIG. 5.

TABLE V

FIFTH HEATING, SERIES PAS. (Fig. 4)

Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
P.M.							
4:00	on			5:22			020
5:00	1100			5:30	1200	*b*	*d*
5:10	1200	021		5:33		019, *C*	*g*
5:20	1200	020, *i*, *g*, *d*	021	5:35	1210(off)	*j*	019, *C*,*b*,*i*

TABLE VI

SIXTH HEATING, SERIES PAS

2.5% Limit (Fig. 4)

Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
12:00 M.	on			1:50	1210	*b*	
P.M.				1:53			*d*
1:00	1000			1:55	1210		*g*
1:25	1200	020		1:58			019, *i*, *j*, *k*, *E*, *C*
1:35			020				
1:45	1200	019, all except *b*		2:00	1220 (off)		*f*, *b*($\frac{3}{4}$ down)

This heating was a check on the fifth heating. *d* again is the lowest deformation member. The molecular per cent is 32.5PbO, $7.5Al_2O_3$ and $60SiO_2$. The chemical analysis gives the weight per cent and the molecular per cent as follows:

	Weight per cent	Molecular per cent
PbO	60.8	31.6
Al_2O_3	7.1	8.0
SiO_2	31.45	60.4

The molecular formula according to the analysis is,

$$PbO : 0.254Al_2O_3 : 1.91SiO_2.$$

The deformation temperature is approximately 1200°F or 650°C.

TABLE VII

SEVENTH HEATING, SERIES PAS (Fig. 2)

Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp in °F	Started	Down
12:00 M.	on			2:10	1230		D
P.M.				2:12			22, 37
1:30	1000			2:15	1250		7, 29
1:45		11		2:18			46
1:50	1200	22, *A*		2:25			16
1:52		46, 37, 29, *D*		2:30	1300	4	
1:56	1210		11	3:00	1400		4
1:57			*A*	6:00	2000	2[a]	
2:00		7, 16					

[a] Some PbO possibly volatilized during such a long heating.

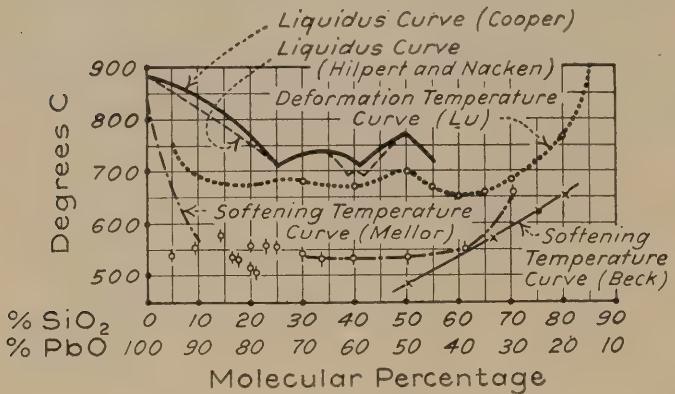

FIG. 6.

This heating developed three binary eutectics, two high in PbO and one high in SiO_2. The deformation temperature curve is shown in Fig. 6, indicating a good agreement with the corresponding eutectics on the liquidus curve developed by Cooper and by Hilpert and Nacken. Mellor's observation though entirely different in nature gave the same result considering the effect of increasing the SiO_2 content. Beck's work was done on the passability of electric current through a granular mixture rather than the measurement of softening temperature.

V. Series ZnO-Al_2O_3-SiO_2(ZAS)

A. S. Watts[1] had developed in his study of Bristol glazes a low fusion mixture with a molecular formula,

$$ZnO : 0.324Al_2O_3 : 0.81SiO_2$$

A series was made up using C.P. materials to check the eutectic. The area investigated in this system was shown in Figs. 5 and 7.

1. First Heating, Series ZAS

Area 2-29-35, 10%. Limit. (Fig. 5.)

As Prof. Watts' eutectic deforms at cones 12-13, the area around this composition was investigated at this temperature. The entire set was heated in a gas-fired kiln. At the end of thirty hours firing, the kiln was shut down between cones 12 and 13. Not a single one was down. Numbers 17, 23, 24, 30, 31 and 32 were the only ones that showed any signs of deformation.

2. Second Heating, Series ZAS (Fig. 5)

Having failed to bring down a single member in the first heating the object now was to locate the range of temperature at which they would probably deform. The six members located from the first heat were put into a gas fired Meker furnace and heated to cones 13-14. From the degree of their deformation, the order can be judged as follows:

23 flattened to a round ball	24 leaned, about $\frac{3}{4}$ down
17 flattened but with top remaining	30 tipped with top melted
31 just touched cone plaque	32 did not deform

From this heating 17 and 23 seemed to have the lowest deformation temperatures. It is then desirable to heat the entire set 2-29-35 to a higher temperature and at the same time study the intermediate members around numbers 17 and 23 within the 5% limit.

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[1] A. S. Watts, *Trans. Amer. Ceram. Soc.*, **18**, 634 (1916).

3. Third Heating, Series ZAS The entire set 2-29-35 heated to cones 12-13 in the first firing were put into a gas-fired kiln again and finished at cones 15-16 in 36 hours of firing. Still none of the cones showed any sign of deformation. All cones showed a cracked surface and some a glassy one. Undergoing such a long soaking fire, the ZnO is undoubtedly volatilized to a certain extent. The shrinkage of the cones was also remarkable as the heating temperature increases agreeing with Libman's[1] statement in his investigation on ZnO bodies. If the cones were heated up more rapidly as in the second heating, there will be less chance for the slow crystallization of ZnO which is probably responsible for the disintegration of the whole mass.

4. Fourth Heating, Series ZAS (5% Limit) Fig. 6 Eleven members were made around 17 and 23 and heated in the Meker furnace. The firing was finished at cones 12-13 with a period of three and one-half hours. From the degree of deformation the order was established as follows:

F	down and started to melt together,	*H*, *C*, *D*, *G*, 17	tipped only
K, *I*, 23	just down	*A*, *B*, *J*	did not deform
E	half down		

Within the 5% limit *F* deforms at the lowest temperature.

5. Fifth Heating, Series ZAS (2.5% Limit) Fig. 7 The limit was narrowed down to 2.5% and nine intermediate members were made from *F*, *K*, *I* and 23. The set was put into the Meker furnace as before and finished at cone 13 after a period of four hours heating. After being removed from the furnace, it was noticed that the cones had been placed too near the bottom. As a result of this, all the cones had their bottoms melted before the top started any deformation, hence the cones had fallen over without passing through a deformation process. From their angle of inclination, however, a difference in deformation is noticeable.

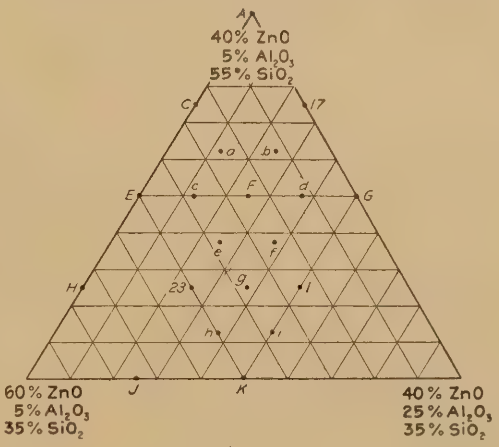

FIG. 7

F, *e*, *K*, *I*	inclined about 45°,
23, *a*, *d*, *c*, *g*	tipped slightly,
h, *i*, *b*, *f*	straight

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[1] E. E. Libman, *Jour. Amer. Ceram. Soc.*, 5, [8] 488-91 (1922).

6. Sixth Heating, Series ZAS

This was a check for the fifth heating. The same members were heated in the Meker furnace and finished at cones 11-12 in three hours. *e* was the first to deform, *F* and 23 followed immediately. When the cones were taken from the furnace at cone 12, the entire set was all deformed. This proved that the deformation temperature was lowest in this area and member *e* can therefore be established as the deformation eutectic of the system ZnO-Al_2O_3-SiO_2 within the 2.5% limit.

The molecular per cent of *e* is 47.5 ZnO, 10 Al_2O_3 and 42.5 SiO_2. The chemical analysis gives the following results:

	Weight per cent	Molecular per cent
ZnO	50.8	46.3
Al_2O_3	14.45	10.5
SiO_2	35.75	43.2

The molecular formula according to the analysis is,

$$ZnO : 0.225Al_2O_3 : 0.906SiO_2.$$

The deformation temperature at cones 11-12 is approximately 1360°C

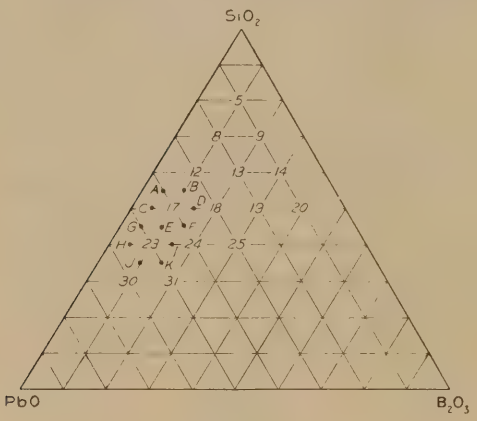

Fig. 8

VI. Series PbO-B_2O_3-SiO_2(PBS)

The B_2O_3 as mentioned before was not introduced as boric acid, but in a frit having the formula 0.972 B_2O_3 : SiO_2.

The area investigated is shown in Figs. 8 and 9.

Table VIII
First Heating, Series PBS. (Fig. 8)
Triangular area 5-17-20, 10% limit
Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
A.M.							
9:00	on			10:50		019	020, 8
10:00(about)		12, 17(missed)	17	10:56	1200		019
10:10	950		12	11:02		018	
10:20	980	18		11:07			018
10:33			18	11:10	1300	14	
10:38	1040	022		11:15		13, 19, 20	
10:40		8	022	11:20	1360	9	19, 14 (broken)
10:42		021					
10:46	1140	020	021	11:25	1390		13, 20

As the members 12, 17, and 18 started deformation before the muffle was barely red, their cones could hardly be seen without any outside source of light.

With special slow heating rate and an electric light inside the furnace the three members 12, 17, and 18 were heated and their deformation behavior observed.

TABLE IX
SECOND HEATING, SERIES PBS
Check on 12-17-18

Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
A.M.				M.			
8:00	on			12:00	880		17
11:00	800			P.M.			
11:10	820			12:10	890	12	
11:50	880	17		12:20	900(off)		

TABLE X
THIRD HEATING, SERIES PBS, 5 % Limit (Fig. 8)
Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
A.M.							
10:40	on			11:48		17	
11:20	400			11:50	810		*E*, 23
11:44		*E*		11:55	820	*A*	17
11:45		23		12:00	830	*B*	*A*

The area around 23 seems to be more interesting and the study of the higher PbO members was made in the next heating.

Eight members around 23 were included in the fourth heating of this Series.

TABLE XI
FOURTH HEATING, SERIES PBS
5% limit (Fig. 8)
Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
12:00 M.	on			1:40			*I*
P.M.				1:42			17
1:00	300			1:50	830	31	
1:30	800			2:00	850	*G*, *H*, 24, 36	
1:32		*K*, 23		2:15			*G*, 31, 36
1:33		*E*		2:20			*H*
1:36	810	*I*, *J*	*E*, 23	2:30	900		24
1:37		17	*K*				
1:39			*J*				

The members, *E*, *K* and 23 were the lowest deformation mixtures within the 5% limit.

TABLE XII
FIFTH HEATING, SERIES PBS
2.5% limit (Fig. 9)
Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
10:30	on			11:35	810	*g*	*f*, *j*
11:20	700			11:36		*a*	23
11:25		*i*		11:37		*e*	*E*, *K*,
11:27		*k*		11:39		*c*, *h*	*a*, *b*, *d*
11:30	780	*d*, *j*	*k*	11:40	830		*e*, *g*
11:32		*f*, *K*, 23	*i*	11:44	840 (off)		*c*, *h*
11:33		*E*, *b*					

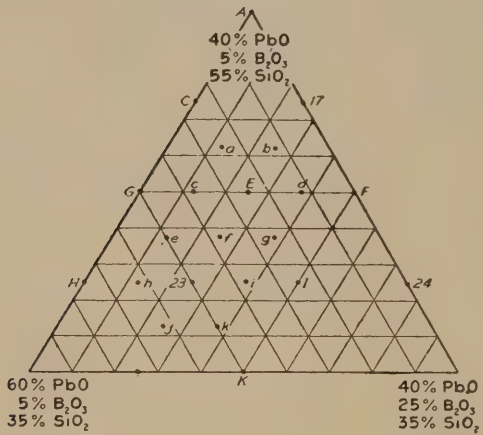

FIG. 9.

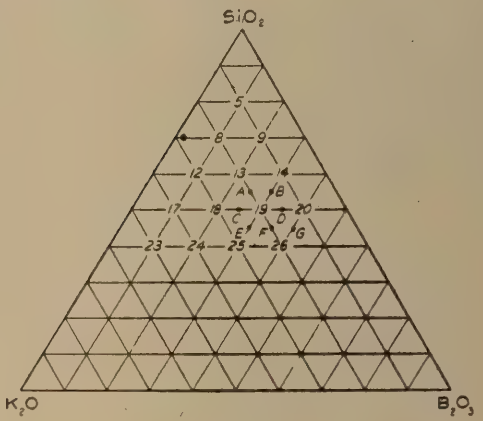

FIG. 10.

TABLE XIII
SIXTH HEATING, SERIES PBS
2.5% limit (Fig. 9)
Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
P.M.				P.M.			
4:00	on			5:50	850	*E*	*j*, *f*
5:30	700			5:52		30	23, *E*
5:36	740	*k*, *i*		5:55	900	31	*K*, *J*
5:40	750	*f*, *j*	*k*	6:00	960		30
5:44	800	*K*, *J*, 23	*i*	6:20	1040		31

The sixth heating is a check for the fifth.

k again leads in deformation and hence is established as the deformation eutectic of this system within the 2.5% limit.

The molecular percentage of the member *k* is 50.0PbO, 37.5SiO_2 and 12.5B_2O_3. The chemical analysis (B_2O_3 from difference) gives the weight percentage and molecular percentage as follows:

	Weight per cent	Molecular per cent
PbO	77.55	49.25
B_2O_3	6.05	12.4
SiO_2	16.4	38.35

The molecular formula according to analysis is,

$$PbO : 0.238B_2O_3 : 0.78SiO_2.$$

The deformation temperature is approximately 780°F or 415°C.

But this is not the eutectic of the entire system PbO-B_2O_3-SiO_2. There will probably be still lower deformation mixtures in the high B_2O_3 area but they are deliquescent on account of their high B_2O_3 content.

VII. Series $K_2O_2B_3O$-SiO_2(KBS)

In making the cones, difficulties were encountered in the use of dextrin and water. The mass containing K_2CO_3 and the melted B_2O_3-SiO_2 mixture takes up water readily and sets into a hard conglomerate before any working could be done. This was not always the case. Most troubles occur in the high K_2O members. Later molasses was found to be a good substitute for dextrin.

The area of investigation in this system is shown in Figs. 10 and 11.

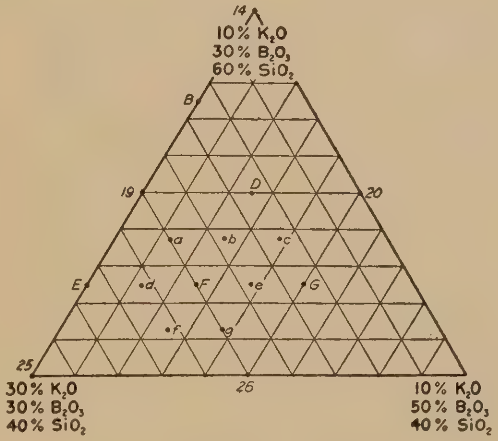

FIG. 11.

TABLE XIV

FIRST HEATING, SERIES KBS

Triangular area 5-17-20, 10% limit. (Fig. 10)

Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
P.M.							
2:40	on			4:35		14	
4:00	1000			4:40	1220	018, 9	19
4:05		022		4:46			14, 20
4:15	1100	021	022	4:49			9
4:20		020	021	4:54	1300	13	018
4:24		18	020	5:10		016, 17	
4:27		019		5:25	1400	12	016, 17
4:30	1180	19, 20	18(bent to a hook)	5:40		014, 8	
4:32			019	5:45	1460(off)		014

In Table XV new members of less silica were included and the per cent limit cut down to five.

TABLE XV
SECOND HEATING, SERIES KBS. (Fig. 10)
Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
A.M.							
9:40	on			11:52			*B*
10:40	800			11:54			018, 14, *A*
11:03	1000			11:56			20
11:26		19		M.			
11:28		019		12:00	1300	017, 25, *C*	*E* (broken)
11:30		14		P.M.			
11:33		*F*, 26		12:05		17	
11:35		*A*, 20		12:13			017
11:37	1180		*F*	12:15		016	17 (shrunk to half size)
11:38		*B*					
11:40	1200		019				
11:42		*D*	26	12:20		24	
11:45			19	12:25		18	
11:48		018		12:30	1400		016
11:50	1250	*E*	*D*	12:45	1450		24

TABLE XVI
THIRD HEATING, SERIES KBS (Fig. 11)
Deformation Data

Time	Temp. in °F	Started	Down	Time	Time. in °F	Started	Down
M.				P.M.			
12:00	on			2:10		*b*	
P.M.				2:12			*F*, *e*
1:00	800			2:15			019, 26
1:30	1000			2:17			*D*, *b*
1:45	1100			2:20	1240	018	*G*
1:50		*c*, *g*		2:28			018
1:56		020		2:30	1300	19	
2:00	1180		020, *c*	2:40		017	
2:05	1200	019, *G*	*g*	2:50	1350		017, 19
2:08		*D*, *F*, *e*, 26		2:55		*a*	

This heating establishes *c* as the deformation eutectic within 2.5% limit.

The third heating is checked by the following run.

TABLE XVII
FOURTH HEATING, SERIES KBS
2.5% limit (Fig. 11)
Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
P.M.				P.M.			
3:00	on			4:55			021
4:30	1000	022		5:00	1200	020, *c*	
4:38			022	5:05		*g*	
4:45	1100	021		5:08		*e*	020, *c*

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
P.M.				P.M.			
5:15		019, 26, *F*	*g*	5:28		*D*	26, *b*
5:18		*G*		5:35			*D*
5:20	1230	*b*	*e*	5:40			019, *G*
5:25			*F*	5:45	1280 (off)	018	

This is a very good check and establishes *c* as the deformation eutectic.

The molecular per cent of member *c* is $15.0K_2O$, $37.5B_2O_3$ and $47.5SiO_2$. But the chemical analysis gives the following results.

	Weight per cent	Molecular per cent
K_2O	23.7	17.6
B_2O_3	37.2	37.0
SiO_2	39.1	45.4

The molecular formula according to the chemical analysis is,

$$K_2O : 2.11B_2O_3 : 2.585SiO_2$$

The deformation temperature is approximately 1200°F or 655°C.

VIII. Series $Na_2OB_2O_3$-SiO_2(NBS)

Molasses was used as a binder but after a few trials dextrin and water were proved equally satisfactory though it could hardly be used with the extremely high Na_2O members.

It was not intended to study the high B_2O_3 members, hence the deformation eutectic developed can only be considered as the eutectic of the area shown in Fig. 12.

The area of investigation in this system was shown in Figs. 12 and 13.

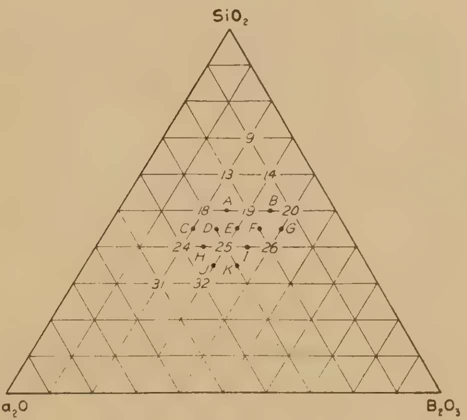

FIG. 12.

TABLE XVIII
FIRST HEATING, SERIES NBS
10% limit (Fig. 12)
Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
A.M.				A.M.			
8:00	on			10:10			13
9:00	800			10:13			32
9:30	1000			10:15		24	019
9:37		022		10:18	1250	018	24
9:45	1100		022	10:25			018
9:55		19, 25, 26		10:30		20	14
9:58		020		10:40			20
10:00		14, 18	020, 25, 26	10:43		017	
10:02			19	10:50	1360 (off)		017
10:05	1200	019, 13, 32	18				

Members 19, 25 and 26 had the lowest deformation temperature.

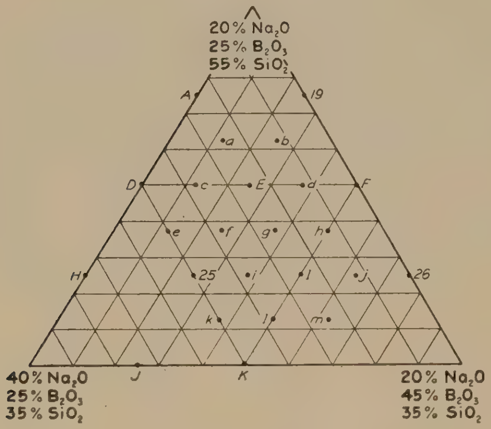

FIG. 13.

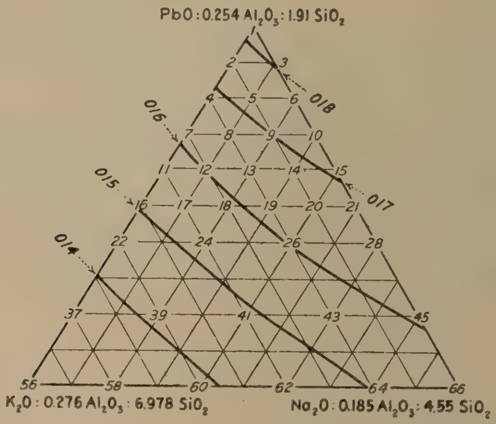
$PbO:0.254\ Al_2O_3:1.91\ SiO_2$
1
2
3
4
5
6
018
016
7
8
9
10
11
12
13
14
15
015
16
17
18
19
20
21
017
014
22
24
26
28
37
39
41
43
45
56
58
60
62
64
66
$K_2O:0.276\ Al_2O_3:6.978\ SiO_2$
$Na_2O:0.185\ Al_2O_3:4.55\ SiO_2$

FIG. 14.

TABLE XIX

SECOND HEATING, SERIES NBS

5% limit (Fig. 12)

Deformation Data

Time	Temp. in °F	Started	Time	Temp. in °F	Started	Down
A.M.			P.M.			
10:40	on		12:15		*E*, 18	
11:10	500		12:20	1100	*J*, *H*, *K*, 25	022
11:45	900		12:25		022, *D*, *G*, 19	*E*, *I*
12:00	1000	*B*, *F*, *I*, 26	12:30		019, *A*	020, *B*, *F*, 19, 26
P.M.						
12:08		022	12:35		*C*, 14	019, *A*, *K*, J, 18, 25
			12:40	1200		*D*, *H*

Members *E* and *I* led in deformation.

TABLE XX

THIRD HEATING, SERIES NBS

(2.5% limit)

Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
A.M.							
10:50	on			12:22	1120	*E*	*i*, *j*
11:35	750			12:24			*b*, *f*, *h*, *E*
11:55	940			12:25		*a*	*l*, *m*, *k*, *K*, 25
12:00	980	*g*, *d*, *h*, *j*, *m*					
P.M.				12:30	1150	18	*c*, *d*, *e*, *F*
12:05	1020	*b*, *l*, *F*, 26		12:35		020, *H*, *J*	*a*, 19, 26
12:10	1060	*c*, *e*, *f*, *i*, *I*, 022	*g*	12:40	1200	*D*, *G*	*H*
				12:45			020, *J*, 18
12:15	1100	*K*	022, *I*	12:48	1220		*D*
12:20		*k*, 19, 25					

This heating establishes member *g* as the deformation eutectic within the 5% limit.

The molecular percentage of the member *g* is $25.0Na_2O$, $32.5B_2O_3$ and $42.5\ SiO_2$. But the chemical analysis gives the weight percentage and the molecular percentage as follows:

	Weight per cent	Molecular per cent
Na_2O	24.2	24.8
B_2O_3	35.2	32.1
SiO_2	40.6	43.1

The molecular formula according to the chemical analysis is,

$$Na_2O : 1.29B_2O_3 : 1.73SiO_2.$$

The deformation temperature is approximately 1060°F or 570°C.

IX. Combination of Deformation Eutectics

As the original object of this investigation was to study the possibility of a synthetic enamel from eutectic combinations, a few combinations of the ternary eutectics developed were studied.

1. PbO-K_2O-Na_2O-Al_2O_3-SiO_2 The first of the series was made on a combination of the eutectic of the lead aluminosilicates developed by the author together with two eutectics of alkali aluminosilicates developed by B. A. Rice.[1]

Molecular Formula	Approx. Deformation Temp .°C
$PbO : 0.254Al_2O_3 : 1.91SiO_2$	650
$K_2O : 0.276Al_2O_3 : 6.978SiO_2$	870
$Na_2O : 0.185Al_2O_3 : 4.55SiO_2$	800

These eutectics were taken as end members and blends were made out from melts of these members. The members studied were shown in Fig. 14.

TABLE XXI
FIRST HEATING, SERIES PKNAS
20% limit (Fig. 14)
Deformation Data

Time P.M.	Temp. in °F	Started	Down	Time P.M.	Temp. in °F	Started	Down
1:00	on			3:20		017, 28	
2:30	1000			3:24		4, 43, 62, 64, 66	15
2:48	1160	020					
2:54			020	3:30	1360	016, 26, 41, 56, 58	017, 28
2:58	1200	019					
3:05		1		3:34			13
3:10		018, 6, 13	019, 1	3:37		24, 39	
3:15	1290	15, 45		3:40		11	4, 45
3:18			018, 6	3:45	1420	015	016, 26

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[1] B. A. Rice, *loc. cit.*, p. 525.

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
3:52			64	4:20		37	22
3:55		22, 60	43	4:25		013	60
4:00	1460		11, 24	4:30			37
4:05			015, 66				
4:08		014	41	4:40	1580		013,58
4:15	1510		39, 62				
4:18			014	4:45	1600 (off)		56

Within the limit studied there is no sign of eutectic formation among the three aluminosilicates. The lead aluminosilicate was the first to deform. To study this a little further the limit was cut down to 10%.

TABLE XXII
SECOND HEATING, SERIES PKNAS
10% limit (Fig. 14)
Deformation Data

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
P.M.				P.M.			
1:30	on			4:15		017, 21	10
3:05	1000			4:20		7, 8, 12, 14, 19, 20	2, 5, 15
3:20	1100						
3:50	1200	019, 1		4:25	1350		017, 9
3:58			1	4:30		016	13
4:00		2, 3, 6	019	4:35			14, 21
4:05		018, 10	3, 6	4:40		11, 16, 17, 18	4, 7, 8, 20
4:10	1300	4, 5, 9, 13, 15	018				
				4:45	1400 (off)		016, 12, 19

From these two heatings it is safe to say that so far as deformation temperature is concerned, there is no eutectic composition detectable by the means employed. The lead aluminosilicates leads all the rest in deformation. The members of high K_2O deform at much higher temperatures than those of high Na_2O. This uniformity was observed throughout the system and is indicated on the triaxial (Fig. 14).

2. PbO-CaO-ZnO-Al_2O_3-SiO_2

As the second of the series of eutectic combinations, the lead and zinc aluminosilicate eutectics developed by the author were taken to combine with the calcium aluminosilicate eutectic developed by Hanna.[1]

Molecular Formula	Approx. Deformation Temp. °C
$PbO : 0.254Al_2O_3 : 1.91SiO_2$	650
$ZnO : 0.225Al_2O_3 : 0.906SiO_2$	1360
$CaO : 0.348Al_2O_3 : 2.489SiO_2$	1240

The members investigated are shown in Fig. 15.

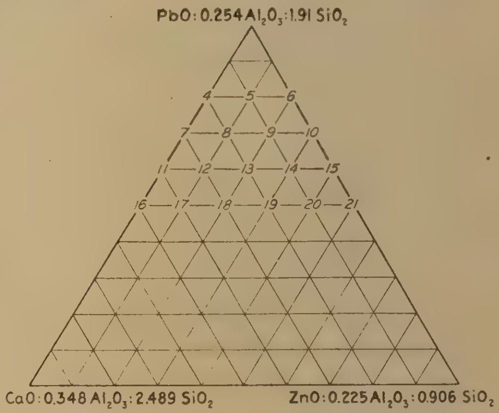
$PbO:0.254Al_2O_3:1.91SiO_2$
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
$CaO:0.348Al_2O_3:2.489SiO_2$
$ZnO:0.225Al_2O_3:0.906SiO_2$

FIG. 15.

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[1] Hanna, *Trans. Amer. Ceram. Soc.* **17**, 672 (1915)

TABLE XXIII

Deformation Data (10% limit)

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
P.M.				P.M.			
1:00	on			3:03			5, 9
2:25	1000			3:05		15	018
2:42	1120	020		3:08		8, 13, 14	4, 15
2:44		6		3:10	1300	21	
2:46		019	020	3:15		7	8, 14
2:49			019	3:20		12, 20	13, 21
2:53		9, 10	6	3:25		017, 11	7
2:55		4, 5		3:30	1380		017, 12
2:58	1220		10	3:35		016, 14, 19	
3:00		018		3:38	1400		016, 20

Similar to the first series of combination, there was no sign of eutectic formation within the area studied. The members of high ZnO deformed at a little lower temperature than those high in CaO.

3. PbO-K_2O-Na_2O-B_2O_3-SiO_2 As the third and last of the series of eutectic combinations, the three borosilicate eutectics developed by the author were used.

Molecular Formula	Approx. Deformation Temp. °C
$PbO : 0.238B_2O_3 : 0.78SiO_2$	415
$K_2O : 2.11B_2O_3 : 2.585SiO_2$	655
$Na_2O : 1.29B_2O_3 : 1.73SiO_2$	570

The members studied are shown in Fig. 16.

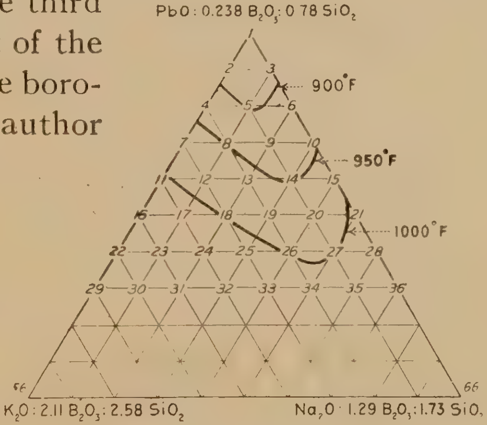
PbO : 0.238 B₂O₃ : 0 78 SiO₂
1
2
3
900°F
4
5
6
7
8
9
10
950°F
11
12
13
14
15
16
17
18
19
20
21
1000°F
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
56
66
K₂O : 2.11 B₂O₃ : 2.58 SiO₂
Na₂O · 1.29 B₂O₃ : 1.73 SiO₂

FIG. 16.

TABLE XXIV

Deformation Data 10% limit (Fig. 16)

Time	Temp. in °F	Started	Down	Time	Temp. in °F	Started	Down
A.M.				A.M.			
10:10	on			11:28		32	21
10:55	700			11:30	1020	22, 30, 31, 36	11, 17, 24, 25, 28, 34, 35
11:05	820	1		11:33			16, 23, 33, 36
11:08		5	1	11:35		29, 56	32
11:10		2, 3, 9		11:38			22, 31
11:12		4, 6, 14		11:40		022, 66	30
11:13		8, 10, 20	2, 3, 5	11:45	1120		022, 29
11:16	900	7, 12, 13, 15, 18, 19, 26, 27	6, 9, 10, 14	11:48			66
11:18		24, 25	4, 8	12:00	1180	020	
11:21	950	21	13	P.M.			
11:23			7, 12, 19, 20	12:05	1200 (off)		020, 56
11:25	1000	11, 16, 17, 23, 28, 33, 34, 35	15, 18, 26, [illegible] 27				

The result of this heating, though very similar to the previous series, was interesting. There was no deformation eutectic among the three borosilicates, but a series of low deformation mixtures was observed when the ratio of Na_2O:K_2O was varying from 2.33 to 4. This relation was shown in Fig. 16 by isothermal lines.

X. Summary

Two aluminosilicate and three borosilicate eutectics were developed within the limit of 2.5 molecular per cent difference. They had the following compositions and deformation temperatures:

(*a*) Molecular Percentage

PbO	ZnO	K_2O	Na_2O	B_2O_3	Al_2O_3	SiO_2	Approx. Deformation Temp. in °C
31.6					8.0	60.4	650
	46.3				10.5	43.2	1360
49.25				12.4		38.35	415
			24.8	32.1		43.1	570
		17.6		37.0		45.4	655

(*b*) Weight Percentage

PbO	ZnO	K_2O	Na_2O	B_2O_3	Al_2O_3	SiO_2
60.8					7.1	31.45
	50.8				14.45	35.75
77.55				6.05		16.4
			24.2	35.2		40.6
		23.7		37.2		39.1

The molecular percentage of these eutectics and several others of similar type developed by previous workers plotted on the triaxial is shown in Fig. 17. A combination of these eutectics was also attempted. By the three combinations made, though not complete, no sign of eutectic formation was found in any of them.

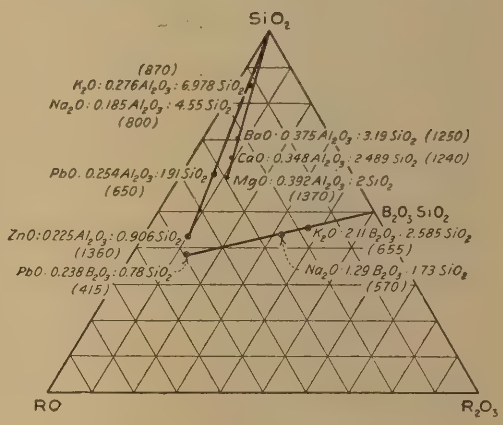

FIG. 17.

XI. Conclusion

A study of the results discloses several promising indications.

Referring to Fig. 17 on which all these eutectics are graphically indicated, we note that a line drawn through the points representing the compositions of the alkali aluminosilicate eutectics and the lead aluminosilicate eutectic would, if extended, terminate in the component SiO_2. Similarly a line drawn through the points representing the compositions of the alkali borosilicate eutectics and the lead borosilicate eutectic would, if extended, terminate in the component $B_2O_3SiO_2$.

A similar relation appears to exist between the eutectics of CaO-Al_2O_3-SiO_2, BaO-Al_2O_3-SiO_2 and MgO-Al_2O_3-SiO_2, the straight line joining these points also terminating in the component SiO_2.

The eutectic of the zinc aluminosilicate lies on the extension of the lead and alkali aluminosilicate line but there is not enough evidence to justify including it in this group.

Again by observing the relative position of the eutectics of lead and alkali aluminosilicates and borosilicates on the triaxial, it is striking to notice that the same order prevails in both series, *i.e.* the order of their positions in the triaxial with regard to the different RO present in the eutectics.

This may be a coincidence between these series of aluminosilicates and borosilicates, but this simple fact will possibly furnish a new phase in the study of thermochemical properties of the silicates.

The recognized viscosities of the aluminosilicates and the borosilicates of the bases above mentioned are in the same order as the above relationship, and this may throw further light on this subject.

The viscosities of the aluminosilicates of the alkali earths are not definitely known and data on this would be necessary in order to consider the possible connection between the behavior of this series and the others.

The deformation temperature of these eutectics, though only approximately determined, offers another interesting feature to this problem. The deformation temperature of the eutectics grouped on the same straight line has either an increasing or a decreasing temperature gradient as the ratio of $SiO_2 : RO$ increases. The PbO, Na_2O and K_2O, both aluminosilicates and borosilicates, belong to the former group while the CaO, BaO and MgO aluminosilicate series belongs to the latter.

It is possible that the deformation temperature is controlled by the combined chemical and physical properties of the RO members with Al_2O_3 and SiO_2. If this assumption is accepted, then it is not unreasonable to assume that this systematic grouping of eutectic compositions is also a function of their corresponding chemical and physical properties. A complete study of this phenomenon will no doubt require a thorough inquiry into the various RO-R_2O_3-SiO_2 systems and a careful observation of their individual thermal behavior.

In the combinations of eutectics studied, the viscosity seemed to be a dominating factor of the resulting melts and their thermal behavior, especially properties like deformation temperature, will probably be overshadowed by the viscosity of the mass. There may be an eutectic of low melting point, but its high viscosity may cause the mass to require so long a time to complete deformation that the temperature has risen above its melting point.

From the results obtained thus far, it is reasonable to expect that in the construction of an enamel or a glass by combination of eutectics, as more RO members or their eutectics were introduced, there will be a point reached when the viscosity of the resulting glass cannot be diminished to any appreciable degree and consequently nothing be gained by the addition of more RO members so far as fusion temperature is concerned.

In studying the various components of an enamel or a glass, the combination of eutectics to determine the most fusible mixtures is one of the logical means of attacking the problem. The most fusible mixture may not necessarily be the most desirable one but fusibility should always be considered as a major factor.

MINERALOGY OF CLAY—I[1]

By J. Spotts McDowell

The Mineral Constituents of Clay[2]

ABSTRACT

A review of the literature on the microscopic examination of clays.

Accurate microscopic identification of the mineral constituents of clay is extremely difficult on account of the smallness of the particles. Relatively coarse grains of clay average .100 mm (.004 inch) in diameter; medium grains .020 to .025 mm (.0008 inch), and fine grains .010 mm (.0004 inch) or less.[3] Moreover, many clays contain much material so fine that the particles cannot be distinguished even with a high power petrographic microscope.

Clay has been defined as a mineral aggregate whose essential constituent is hydrated silicate of alumina, and which has certain physical properties. The minerals of this aggregate can be thought of as belonging in two classes: (1) essential constituents, and (2) accessory constituents. Variations in the relative amounts, composition and physical condition of these constituents impart to each type of clay its characteristic properties.

The term "essential constituents" as used here, will refer to those minerals which constitute what is generally spoken of as the "clay base." Unless some one of these minerals is present in amounts sufficient to give specific properties to the mineral aggregate, the latter cannot properly be called a clay. In any given clay, the essential constituent may consist of one mineral or of more than one; it may be mainly crystalline or mainly colloidal; it may comprise nearly the entire clay body, or it may be present in subordinate amounts. The microscopic studies of Galpin[2] and Somers[3] have shown that kaolinite and hydromica are the most important of the essential minerals. The common assumption that kaolinite is the only basic mineral of all highly aluminous clays is not correct. In some clays the base is mainly kaolinite; in most refractory clays, the base is a mixture of kaolinite and hydromica; the great bulk of many clays is hydromica. Halloysite is the base of a very few; other hydrous silicates of alumina have been mentioned as possible clay bases, but they are probably of slight or merely local importance.

The major accessory constituent in most clays is quartz. This is present in nearly every clay, and varies in amount from less than 1%

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[1] Received November 9, 1925. For references in this paper see Bibliography, on p. 60.

to as much as 60%. Contrary to general belief, feldspar is not an important constituent of most refractory clays, and is not often identified under the microscope.[17]

The minor accessory constituents of refractory clays consist of a wide variety of minerals. Some of these are found in small proportions in nearly all clays; others are rarely present. Some of the more common minerals are pyrite, siderite, limonite, rutile, epidote, tourmaline and diaspore.

Essential Constituents

Kaolinite Kaolinite has the theoretical formula $Al_2O_3.2SiO_2.2H_2O$ corresponding to 39.5% Al_2O_3, 46.5% SiO_2, and 14% H_2O. Its hardness is 2 to 2.5 and specific gravity 2.6 to 2.63. The color is usually white. Kaolinite commonly occurs in plastic clay-like masses; under the microscope it is seen to consist of scales or plates which are often grouped in fan-shaped forms. It is always of secondary origin, and is assumed to have been derived in most cases from feldspar, although its possible derivation from numerous other minerals has been suggested.[7]

The mineral kaolinite can be identified in clays microscopically by its characteristic single and double refraction, and by its form. It occurs in single plates or scales, sometimes in fan-shaped aggregates or worm-shaped bunches. When very fine, it appears as minute transparent plates.

Colloidal Materials Many clays contain material which is so fine that the particles cannot be detected under the microscope. This material is assumed to be colloidal. From the index of refraction it has in some cases been identified as kaolinite. Some very plastic clays contain a large amount of colloidal matter.

Halloysite Halloysite is a clay-like mineral with a hardness of 1 to 2; specific gravity 2.0 to 2.2; luster, pearly or waxy. Its chemical composition is like that of kaolinite except that it contains more water (19.6%). The clay known as Indianaite from the Huron district, Indiana, and a few other clays, have been shown to contain large amounts of halloysite.

Mica A common constituent of clays is sericite, which is a fine scaly variety of muscovite mica, occurring in fibrous aggregates. It is believed to have been derived in most cases from the decomposition of feldspar.

In nearly all clays[2,3] the microscope reveals the presence of crystalline minerals which are distinctly micaceous, and whose single and double refraction are between those of muscovite and those of kaolinite. These minerals frequently occur in plates and fan-shaped bunches similar to the fans of kaolinite, but of larger size. These crystals have been called "hydromica" by Galpin and Somers.[2,3] In a single section crystals can sometimes be seen forming an unbroken series whose birefringence varies from that of muscovite to that of kaolinite. Galpin has reported that prisms and plates of kaolinite frequently show ribs or plates of mica intergrown with those of the kaolinite. These ribs show every grade of variation from muscovite to kaolinite.

According to Somers, it is assumed that there is an isomorphous gradation from sericite to kaolinite with a gradual loss of potash and addition of water, and that hydromica represents the transition stage with kaolinite as the final product.[3] Hickling[13] refers to the established fact that muscovite does become hydrated, when immersed in pure water or water saturated with CO_2. He believes that the mica changes directly to kaolinite in the clay, for the following reasons:

1. There was mica but no kaolinite in feldspar.
2. There is no difference in form between the mica and kaolinite.
3. Prisms were observed which were mica at one end and kaolinite at the other.

A comparison of the chemical formulas and analyses of orthoclase feldspar, muscovite and kaolinite is of interest in showing that muscovite is intermediate in composition between the other two.

TABLE I

		Al_2O_3	SiO_2	K_2O	H_2O
Molecular Ratio	Orthoclase	3	18	3	0
	Muscovite	3	6	1	2
	Kaolinite	3	6	0	6
Chemical Analysis	Orthoclase	18.4%	64.7%	16.9	0%
	Muscovite	38.5	45.2	11.8	4.5
	Kaolinite	39.5	46.5	0	14.0

In both orthoclase and muscovite a portion of the potash is usually replaced by soda.

Major Accessory Constituents

Quartz (SiO_2) Nearly all clays contain some free silica in the form of quartz. In the residual clays quartz is particularly abundant; in pure kaolins and in some fire clays its percentage is negligible. The size of the individual grains varies in different clays, and in a few can be seen with the naked eye. Amorphous silica is found in some clays.

Diaspore The major accessory constituent of the nodule clays of Pennsylvania and of the burley clays of Missouri is diaspore ($Al_2O_3.H_2O$) instead of quartz. It occurs in the form of scattered grains.

Minor Accessory Constituents

Iron Compounds Common iron minerals in clays are pyrite (FeS_2), siderite ($FeCO_3$), and ferric oxide, anhydrous hematite (Fe_2O_3), or in various stages of hydration, limonite ($2\ Fe_2O_3.3H_2O$) and other minerals). Other iron-bearing minerals such as biotite mica, hornblende and magnetite (Fe_3O_4) occur infrequently.

No clay is free from iron, which is the principal coloring agent in fired clay. White-firing clays contain from a few hundredths of a per cent to over 1% of iron; buff-firing clays from .5% to 4 or 5%; red-firing clays, 4 to 7%. The iron minerals may be present in either the colloidal or granular condition. Colloidal or disseminated iron produces an even color on firing; grains of iron minerals form iron spots. Ferric oxide and hydroxide tend to be disseminated throughout a clay; iron carbonate may be either disseminated or in grains; pyrite invariably occurs in granular form.

The fire clays contain most of their iron in the form of siderite or pyrite. However, where they are exposed to the air or to percolating waters, as in stock piles or on the outcrop of clay beds, these minerals eventually change to limonite. Siderite in fire clay occurs in the form of microscopic grains and as a film coating other minerals. Pyrite (Fe 46.6%, S53.4%) which is yellow can often be seen by the naked eye, and is called "sulphur" by clay miners. It occurs in large lumps, small grains or cubes, and in flat rosettelike forms.[7] This mineral is the cause of much difficulty in the firing of clay ware. Hydrated ferric oxide is most abundant in surface clays, or in the weathered outcrops of bedded deposits.

Other Minerals Nearly all clays contain some rutile (TiO_2). It sometimes occurs in prisms or grains .015 to .020 mm (.0006 to .0008 inch) in diameter,[3] more often as grains or needles .001 to .010 mm (.00004 to .00040 inch) in diameter and 5 to 6 times as long as wide. The number of these grains is large, but they represent only a small quantity of rutile. Minerals commonly found in clay, but in very small amounts, are tourmaline (a complex silicate of boron and aluminum); epidote (a hydrated lime-iron aluminum silicate); zircon ($ZrO_2.SiO_2$); and titanite ($CaO.TiO_2.SiO_2$). Other clays have been reported to contain varying amounts of calcite ($CaCO_3$), gypsum ($CaSO_4.2H_2O$), glauconite (a hydrated silicate of potash and iron) and garnet.

Constitution of Some Typical Clays

Flint Fire Clay Typical flint clays examined by Galpin were very finely crystalline, consisting of kaolinite in prisms, fans, and vermicular forms. The prisms were not infrequently ribbed with hydromicas. Considerable difference was observed in the grain-size of flint clays from different districts. In that from Woodland, Pa., the kaolinite grains averaged .005 to .010 mm (.00020 to .00040 inch) in diameter, although there was much finer material. In normal flint clays other minerals are scarce, but always present. Badly corroded grains of quartz up to .090 mm (.0036 inch) diameter were observed; also a few zircon and tourmaline grains, rutile needles and muscovite plates.

Semi-plastic Fire Clay The semi-plastic fire clay which occurs in the same bed with the flint clay at Woodland, Pa., is described as a felt of mineral plates of .005 to .200 mm (.00020 to .008 inch) diameter. Three prominent types of mineral grains were observed:

1. Large muscovite plates .100 to .250 mm (.004 to .010 inch) in diameter; conspicuous, but only small part of the clay.
2. The bulk of the clay consists of plates smaller than the above in a confused felt-like mass. They are believed to be hydromicas.
3. Considerable kaolinite in prisms, fans and plates is present; ribs of hydromica are common in the plates.

Quartz, zircon, tourmaline and rutile are present in small amounts.

Plastic Fire Clay In the plastic fire clay examined by Galpin, hydromica was the most common mineral. None of the plates and grains exceeded .020 to .025 mm (.0008 to .0010 inch) in diameter; much of the clay was too fine to determine with the microscope.

Comparison of Fire Clays According to Galpin,

> Comparison of the flint clays and their associates with other highly aluminous clays, shows that the main difference is in texture. In the flint clays the kaolinite crystals are knit together so tightly that when the clay is crushed they break out in aggregates rather than as individuals. In the semi-plastic clays, the crystals though larger than in the flint clays, are not so tightly interlocked and so become separated in grinding, producing some plasticity. In the plastic clays the crystalline particles are smaller and at the same time more or less separated.

It appears also that in clays of the fire-clay type the plastic clays contain more hydromica and less kaolinite than do the flint clays, and more colloidal material.

Other Clays Somers[3] has made a microscopic examination of over 100 samples of American clays. Two minerals present in all were kaolinite and hydromica. In the white clay of Georgia, he found that kaolinite is usually abundant; hydromica, common; quartz, zircon and rutile scarce. In the white clays of South Carolina kaolinite is abundant, hydromica, common; quartz, variable; rutile, fairly common; zircon, scarce. The residual clays from the Cambrian schist of eastern Pennsylvania contain abundant kaolinite; moderate to abundant hydromica; common to abundant quartz; rutile is common; zircon, tourmaline, epidote and titanite were observed but are scarce.

In an examination of china clays Schurecht[11] found that English china clay consists mostly of distinct crystalline plates and platy aggregates of kaolinite, whereas Georgia and South Carolina clays are constituted largely of colloidal kaolin aggregates. He attributes the distinctive properties of the English clay to its crystalline texture.

Harbison-Walker Refractories Co.,
Pittsburgh, Pa.

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RATIONAL ANALYSIS OF CLAY—II[1]

By J. Spotts McDowell

Rational Analysis

ABSTRACT

A review of the literature on the rational analysis of clays. The methods of determining the rational analysis are shown to be inaccurate.

Ultimate and Rational Analysis Compared

The object of the "ultimate analysis" of clay is the determination of the various constituent oxides, such as silica, alumina, iron oxide, titania, lime, magnesia, alkalis and combined water. From a knowledge of the relative proportions of these oxides, certain inferences can be drawn regarding the properties of the material. Clays free from iron fire white, while iron tends to produce a buff or red color upon firing. Iron, lime, magnesia and alkalis tend to lower the melting point; hence a high content of these impurities is an indication of low refractory value. However, the ultimate analysis is unsatisfactory as a guide in judging the physical properties of a clay; for clays of similar analysis often exhibit decidedly dissimilar working and firing behavior.

Clays are mineral aggregates, and their characteristic properties depend upon the relative amounts, composition and physical condition of the constituent minerals. The ultimate analysis does not indicate what these minerals are. Iron, for example, is reported merely as "Fe_2O_3"; yet it may be present as siderite, as pyrite, as disseminated limonite, or in other minerals, each of which may have a different effect upon the properties of the clay. Silica in combination with other elements will exert an altogether different influence from uncombined silica.

Ceramists have long felt the need for a method which will resolve a clay into its mineral components, and have devised for this purpose the so-called "rational analysis." The earlier investigators made the rational analysis by direct laboratory processes; at present the view is generally held that calculation of the rational analysis from the ultimate analysis is preferable. The results of both methods are erroneous and more or less misleading, as they are based upon assumptions which are not in accordance with facts now known. The only way in which the constituent minerals can be positively determined is through microscopic studies. These, however, are only roughly quantitative, and do not give the exact proportion of the various minerals.

Methods of Rational Analysis

The methods of the rational analysis are based upon the assumption that clay consists mainly of "clay substance," or kaolinite, quartz and unde-

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[1] Received November 9, 1925. For references in this paper see Bibliography, p. 64.

composed feldspar. Laboratory processes have been devised for separating clays into these fractions, through treatment with various strong reagents, particularly hydrochloric and sulphuric acids and alkali hydroxides.

H. S. Washington states,

> Following Mellor, the essential features of the 'rational' analysis are: digestion of the clay with hot, concentrated sulphuric acid and subsequent washing alternately with alkali and hydrochloric acid, to remove the 'clay substance'; this may be preceded by treatment with hot alkali to remove soluble silica, or with dilute hydrochloric acid, to remove the carbonates; and it may be followed by evaporation of the residue with hydrofluoric acid to remove quartz and other silica, and determination of the alumina, which is used as a basis for the calculation of the feldspar present.[6]

Various writers who apparently accept the assumptions upon which the rational analysis is based, nevertheless consider the laboratory methods faulty. The objections are these:[6] the different feldspars differ in solubility in the chemical reagents; some are quite insoluble, others readily soluble. Kaolin itself varies in its resistance to the reagents, as do the different kinds of silica which may be present. Other important factors which influence the rate of solution of the minerals are size of grain, the concentration of the reagents, the length of time and the temperature of treatment. According to Washington, the methods are

> scarcely susceptible of yielding satisfactory duplicate results except by chance, and even satisfactory duplication of results cannot be regarded as evidence, still less as proof, of their correctness, when the methods are seriously faulty.

Various writers maintain that the rational analysis can be more accurately determined by calculation from the ultimate analysis than by laboratory determination. In the calculation, potash is regarded as a derivative of orthoclase feldspar, and from the potash content the amount of orthoclase is calculated. Soda is assigned to albite; lime usually to anorthite; the remainder of the alumina, after the three feldspars

TABLE I

Ultimate Analysis		Rational Analysis Laboratory Determinaton		Rational Analysis Calculated[a]		
SiO_2	62.40	Clay Substance	66.33	Kaolinite		61.92
Al_2O_3	26.51	Feldspar	18.91	Orthoclase	5.56	
Fe_2O_3	1.14	Quartz	15.61	Anorthite	2.74	
CaO	.57					
MgO	.01		100.85	Total Feldspar		8.30
Alkalis	.98			Quartz		28.80
Loss on Ignition	8.80			Limonite		1.26
	99.91					100.28

[a] Alkalis assumed to be K_2O.

have been satisfied, to kaolinite; any silica above that required for the feldspars and kaolinite is assumed to be quartz. Iron oxide is calculated as limonite.

The two methods of determining rational analysis often exhibit considerable difference in the results, as shown by the references.[1, 6]

The methods of rational analysis depend upon assumptions regarding the constitution of clay which are not supported by microscopic evidence at least so far as refractory clays are concerned. Most of these clays consist mainly of hydromica, kaolinite and quartz, and not of feldspar, kaolinite and quartz.[12] Galpin has determined microscopically that a semi-plastic clay from Woodland, Pa., consists mainly of hydromica and kaolinite, with small amounts of muscovite, quartz, rutile, zircon and tourmaline. No feldspar was observed. However, according to the calculated rational analysis, this clay appears to have the following constitution:

Kaolinite	73.9%	Rutile	3.2
Feldspar	11.4	Limonite	2.3
Quartz	9.2		
		Total	100.0

An accurate quantitative calculation of the mineral constitution of a clay cannot be made even by making use of a microscopic study and the ultimate analysis. The hydromica introduces considerable difficulty, as it appears to be not a definite mineral, but an isomorphous series between kaolinite and muscovite.

Wohlin[13] has analyzed certain earthy materials by determining the time-temperature curves of small samples heated in an electric furnace. Different types of materials were found to have distinctive curves. The lags were usually due to the evolution of water, the rapid rises to polymerization. By this method bauxite ($Al_2O_3.2H_2O$) was proved to be a mixture of gibbsite ($Al_2O_3.3H_2O$) and diaspore ($Al_2O_3.H_2O$). Perhaps this method can be applied further, by using it in conjunction with microscopic studies for the calculation of rational analysis.

Quantitative knowledge of the constitution of a clay, even if obtainable, would not be sufficient information upon which to predict its various properties. Much depends upon size of grain of the component minerals, and upon the proportion of colloidal matter.

Excess Silica The ratio of silica to alumina, and the amount of fluxing oxides, can be used as a crude index of the refractory quality of a clay. A few ceramists make use of the term "excess silica" or "free silica" to represent all of the silica above that required by the ratio $Al_2O_3 : 2\ SiO_2 = 102 : 120$. This procedure seems to be justified, since kaolinite, muscovite and hydromica are the only minerals present in most clays which contain a large percentage of alumina; and in each of these the ratio of alumina to silica is $Al_2O_3 . 2SiO_2$, or 102 : 120. The "excess silica" therefore represents the amount of silica present which is not a part of some one of these minerals; it is largely quartz, but may be in part combined with some of the minor accessory minerals. The iron oxide, titania, lime, magnesia and alkalis may be grouped as "fluxing oxides." These decrease the refractoriness of a clay more when the amount of "excess silica" is high than when it is low.

The diasporitic clays contain "excess alumina" instead of "excess silica."

A specimen calculation of "excess silica," applied to the analysis quoted above is here given:

SiO_2	62.40	
Al_2O_3	26.51	
Fe_2O_3	1.14	Fluxing Oxides 2.70
CaO	.57	
MgO	.01	
Alkalis	.98	
TiO_2	not determined	
Loss on Ignition	8.80	

$$\text{Silica combined with alumina} = 26.51 \times \frac{120}{102} = 31.19\%$$

$$\text{"Excess silica"} \qquad 62.40 - 31.19 = 31.21\%$$

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ORIGINAL PAPERS

AN ULTRAMICROSCOPIC MOTION PICTURE STUDY OF THE RELATION OF COLLOIDAL CONTENT AND PLASTICITY IN CLAYS[1]

BY WESLEY G. FRANCE

ABSTRACT

Many attempts have been made to account for the plasticity of clay on the basis of colloidal content. If these are warranted then one should find characteristic differences in the colloidal fractions of clay suspensions, when examined ultramicroscopically. Furthermore these differences should serve as an indication of the plasticity. Ultramicroscopic motion pictures were taken of the colloidal fractions of the aqueous suspensions of four clays having different plasticities. Marked differences were found in each instance, which indicated the relative order of the decreasing plasticity of the clays examined to be: English china clay; South Carolina kaolin; North Carolina kaolin; and fireclay semi-flint. These results tend to support the idea that a definite relation exists between the colloidal content of a clay and its plasticity. Suggestions with reference to the extension of this work are made.

A. B. Searle[2] states that "Plasticity may be defined as that property of a material which enables it to change its form without rupture, the new shape being retained when the deformatory force is removed." From a practical consideration, a clay must also possess "binding power" in addition to the above property in order to be considered plastic, at least by most clay workers; however, the term has been used rather loosely, in some cases to designate "binding power" and in

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Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Columbus, Ohio. February, 1925.

[1] Received December 22, 1925.

[2] Third Colloid Report. Brit. Assoc. Advancement of Sci. **124A** (1920).

others in the strict sense of the definition quoted. The work of Bingham[1] has done much towards making a better understanding of plasticity, especially in emphasizing its complex nature, as expressed in the conclusions arrived at concerning its two fundamental properties "yield value" and "mobility." These conceptions will doubtless prove to be of considerable value in the study of the plasticity of clays.

Despite the fact that plasticity has long been regarded as one of the most important properties of clay and has been the subject of many investigations, no adequate explanation has yet been offered for it.

Numerous attempts have been made to account for the plasticity of clays on the basis of the colloidal content. Schloesing[2] in 1874 thought that he detected, in clay, an amorphous material, corresponding in composition to kaolin, having colloidal properties, and to the presence of which he attributed the plasticity. Seger[3] expressed the opinion that the plasticity was, perhaps, due to the molecular arrangement of the fine particles of a special form of hydrated aluminium silicate existing in the clay.

Later Rohland and others were led to somewhat similar conclusions.[4] Among those who have opposed the colloid theory of plasticity are H. Le Chatelier[5] who held the presence of fine crystalline lamellae responsible for it, and in support of this opinion showed that mica and glauconite when ground fine enough became plastic. Similarily A. Atterberg[6] demonstrated that $BaSO_4$, CaF_2, $BaCO_3$, $SrCO_3$ and minerals that split into fine scales or plates, when sufficiently finely ground in the presence of water, also became somewhat plastic. R. C. Purdy[7] stated "plasticity is the result of purely physical conditions and properties, adsorption, solution, molecular attraction and high surface tension."

From a consideration of the foregoing references it is apparent that the term "colloid" has been used, at least by many of the earlier investigators, in the same sense as that originally intended by Thos. Graham, namely, to indicate a kind, rather than a state of matter. When used in the latter and more modern sense many of the objections are met. Thus the statement of R. C. Purdy, quoted above, is not out of harmony with the fundamental conceptions of the colloidal state of matter, when we refer to the colloidal content of a clay as being that fraction made up of particles within colloidal dimensions, approximately between the limits 0.1μ–$1\mu\mu$, since the suspension of such particles in most fluids gives rise to stable systems possessing large surface area and consequently great surface energy accompanied by marked adsorption effects.

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[1] Fluidity and Plasticity. McGraw-Hill Book Company, 1922.

[2] *Comptes rendus*, **79,** 376, 473 (1874).

[3] *Thonindustrie Ztg.*, **2,** 37 (1877).

[4] P. Rohland, *Zeit. Anorg. Chem.*, **31,** 158 (1902); *Z. Electrochem.* **15,** 540–4 (1909); *Sprechsaal*, **42,** [1–3], 655–57 (1909); *ibid.*, **47,** 129–36 (1914); *Kolloid Zeit.*, **13,** 62–3; (1913); Van der Bellen, *Chem. Zeit.*, **27,** 443 (1903); A. S. Cushman, *Trans. Amer. Ceram. Soc.*, **6,** 65 (1904); *ibid.*, **8,** 180 (1906); H. E. Ashley, *Trans. Amer. Ceram. Soc.*, **11,** 530–95 (1909); Bureau of Standards, *Tech. Papers*, **23**; A. V. Bleininger, *Jour. Ind. Eng. Chem.*, **12,** 436–38 (1920); G. A. Bole, *Jour. Amer. Ceram. Soc.*, **5,** 469 (1922); J. W. Mellor, *Trans. Ceram. Soc.* (Eng.), **21,** 91–103 (1921-22).

[5] Van Bemmelen, Godenboek, pp. 163–72.

[6] *Z. Angew. Chem.*, **24,** 928–9 (1911) and R. Rieke, *Ceramique*, **15,** 87 (1912).

[7] *Jour. Amer. Ceram. Soc.*, **5,** 475 (1922).

Since the present paper has for its object the ultramicroscopic investigation of the colloidal content of several clays with the view of determining what, if any, relation may exist between plasticity and colloidal content, further discussion of the various theories of plasticity will be deferred until a later paper.

As already shown it is not difficult to find many references in the literature which state that the colloidal content of a clay determines its plasticity. If such statements are warranted, then one might reasonably expect to find characteristic differences in the colloidal fractions of suspensions of clays having different plasticities, when examined with the ultramicroscope, since the particles constituting these fractions are too small to be observed by other means. P. Ehrenberg and G. Given[1] and also J. Alexander[2] have made use of the ultramicroscope in the study of clays. In neither case, however, was any direct correlation made between the observed results and the plasticities of the clays.

In the present work ultramicroscopic motion pictures were made in order to facilitate the comparison of the colloidal content of the clays investigated.

The value of the motion picture camera in colloidal investigations was early demonstrated by Victor Henri[3] in his motion picture study of the Brownian Movement of rubber latex particles by means of a high power microscope. Two or three years later Jean Comandon[4] combined the motion picture camera with the ultramicroscope and ultramicroscopically photographed minute organisms and particles of colloidal dimensions.

Little use, however, was made of the motion picture camera in this connection until employed by Darke, McBain and Salmon[5] in a study of soap structures, and by W. G. and H. C. Eddy[1] in a study of emulsions. The first investigation in which the motion picture camera and ultramicroscope were combined in this laboratory was in a study of the Brownian Movements of basic lead carbonate suspensions and of red gold sols both in the presence and absence of gelatin. An account of this work was prepared for the April, 1924, meeting of the American Chemical Society, and an abstract published in the Abstracts of the Inorganic and Physical Chemistry Division.[2] Due however, to the inability of the writer to attend the meeting the paper was presented by title only. Subsequently E. O. Kraemer presented a paper entitled "Studies with the Kinoultramicroscope," at the Second Colloid Symposium[3] in June, 1924, and more recently E. P. Wightman and A. P. H. Trivelli[4] have published a motion picture study of rubber latex particles.

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[1] *Kolloid, Zeit.*, **17**, 33–7 (1915).

[2] *Jour. Amer. Ceram. Soc.*, **3**, 612 (1920).

[3] *Societe Francaise de Physique Bulletin des Seances*, **4**, 45, 61 (1908).

[4] F. A. Talbot, "Practical Cinematography and Its Applications," p. 169, J. B. Lippincott, 1913.

[5] *Proc. Roy. Soc.*, (London) **98A**, 395 (1921).

Apparatus

In our earlier work a Pathe Field Camera employing standard 35 mm. motion picture film was used. Because of the inconvenience encountered in the finishing of this film with the limited dark room facilities at hand, attempts were made to use one of the smaller cameras employing 16 mm. film. The camera finally selected was a Bell and Howell Filmo camera provided with an F 3.5 lens and using 16 mm. Cine Kodak Film. The remainder of the apparatus consisted of a Siedentopf Cardioid Ultramicroscope, a cooling cell, a direct current arc lamp, and an adjustable support for the camera. The arrangement of this apparatus is shown in Fig. 1, in which *A* is the arc lamp, *c* the cooling cell, *M* the quartz chamber containing a few drops of the colloidal system, *K* the camera and *s* the adjustable support.

As the camera was not designed for microscopic work the following method of focusing was adopted. When the field to be photographed was found, a brass cylinder *L*, (2 cm.×6 cm.), supporting a ground glass was placed on the ocular in the position indicated in Fig. 1. The image of the field was then focused on the ground glass, after which both the cylinder and ground glass were removed. A shorter brass cylinder *L′* was then screwed into the lens mounting of the camera *K* in place of its regular lens, the optical system of the ultramicroscope serving in its stead. The length of the cylinder *L′* was such that when fitted snugly against the shoulder of the lens mounting the distance from the outside end of the cylinder to the film in the camera was exactly 6 cm., that is, the length of the cylinder *L*. Without changing the focus obtained with cylinder *L*, the camera was brought into the position shown in Fig. 2, such that the end of *L′* just came in contact with the top of the ocular, fine adjustment being made by means of the slow motion screw *B*. In this position then the film within the camera occupied the same relative position as the ground glass *G* of Fig. 1 on which the image had been previously focused. The pictures were then taken by simply pressing the button *D*, releasing the automatic spring driven motor of the camera. The films were developed with alkaline pyrogallic acid and fixed in a chrome alum bath, washed in running water and air dried. In addition to the cardioid condenser and quartz chamber, the optical system of the ultramicroscope consisted of a glycerine immersion objective (num. apert. 0.85) and an orthoscopic ocular (F 15 mm.). In some instances photographs were made using the regular camera lens; this simply necessitated the use of a shorter brass tube which was screwed onto the lens collar, and the same procedure followed as already given.

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[1] *Jour. Ind. Eng. Chem.*, **13,** 1016 (1921).

[2] Abstracts of papers to be presented before the Division of Inorganic and Physical Chemistry at the Washington Meeting, No. 30.

[3] Colloid Symposium Monograph, **2,** 57 (1925).

[4] *Jour. Ind. Eng. Chem.*, **17,** 164 (1925).

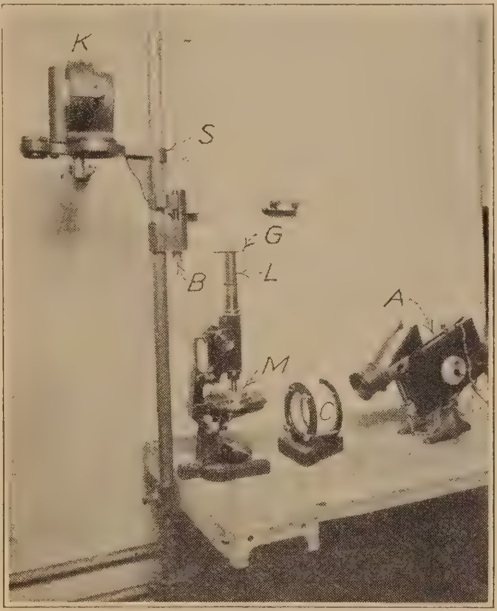

FIG. 1.—Arrangement for focusing

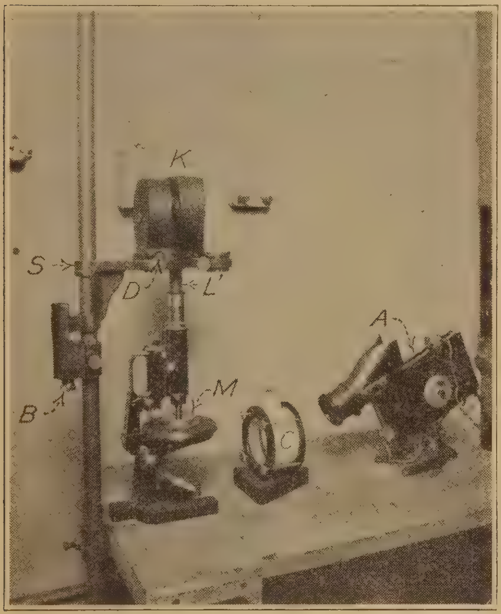

FIG. 2.—Camera in position for taking pictures.

Clays Studied

The clays selected for investigation were an English china clay, a North Carolina kaolin, a South Carolina kaolin and a fireclay semi-flint. Aqueous suspensions of these clays, having a concentration of about 0.1 gram per cc. were furnished by G. A. Bole and H. C. Harrison of the Columbus Station of the Bureau of Mines. The colloidal fractions were obtained in the following way. 0.5 cc. of the thoroughly shaken suspension was placed in a 20 cc. test tube; 15 cc. of distilled water were then added, and after vigorous shaking the test tube was set aside and the contents permitted to settle undisturbed for four hours. At the end of this time the top cc. was removed and diluted ten times. A few drops of this suspension were then placed in the quartz chamber, and the chamber mount *M* placed in the position shown in Figs. 1 and 2. A field was selected and the procedure as already outlined was followed. Three different aqueous suspensions of English china clay were studied: one untreated, one made slightly alkaline with NaOH, and one slightly acid with acetic acid.

Figures 3, 4 5, 6, 7 and 8 are photographic prints of the negatives obtained. The number of light areas can be taken roughly as an indication of the quantity of colloidal material present, and the size of the individual areas can likewise be taken as an indication of the tendency for flocculation.

Figure 3 is the print of the untreated English china clay. This shows a considerable number of large light areas indicating a high colloidal content, and high plasticity based, of course, on the assumption that the colloidal content bears a direct relation to the plasticity of a clay.

Figure 4 is that of the English china clay made slightly alkaline. The decrease in size of the light areas indicates the deflocculating action of the NaOH.

Figure 5 is that of the English china clay made slightly acid with acetic acid. The appearance of only small areas in the field, is doubtless due to the flocculating action of the acid, which produced aggregates of particles exceeding ultramicroscopic dimensions, which settled out and were therefore not included in the colloidal fraction.

Figure 6 is the South Carolina kaolin. Judged by the same standards as Fig. 3, one would conclude that it had almost as high a colloidal content and perhaps about the same or possibly a little less plasticity than the English china clay. From similar considerations, Fig. 7, which represents the North Carolina kaolin, is unquestionably lower in colloidal content and would likewise be less plastic than either of the other clays. Fig. 8, the fireclay semi-flint, would be the least plastic having a much smaller colloidal content than the others. The four clays would therefore be arranged in the order of decreasing plasticity as follows: English china clay; South Carolina kaolin; North Carolina kaolin; and fireclay semi-flint. With the possible interchange of the first two clays, the above is no doubt the correct order of decreasing plasticity. Since, however, the plasticities of these clays were not measured, it is of course impossible to state just what the correct order should be.

It is evident from this work that an ultramicroscopic examination of the colloidal fractions of the clays, reveals characteristic differences

FIG. 3.—English china clay (untreated).

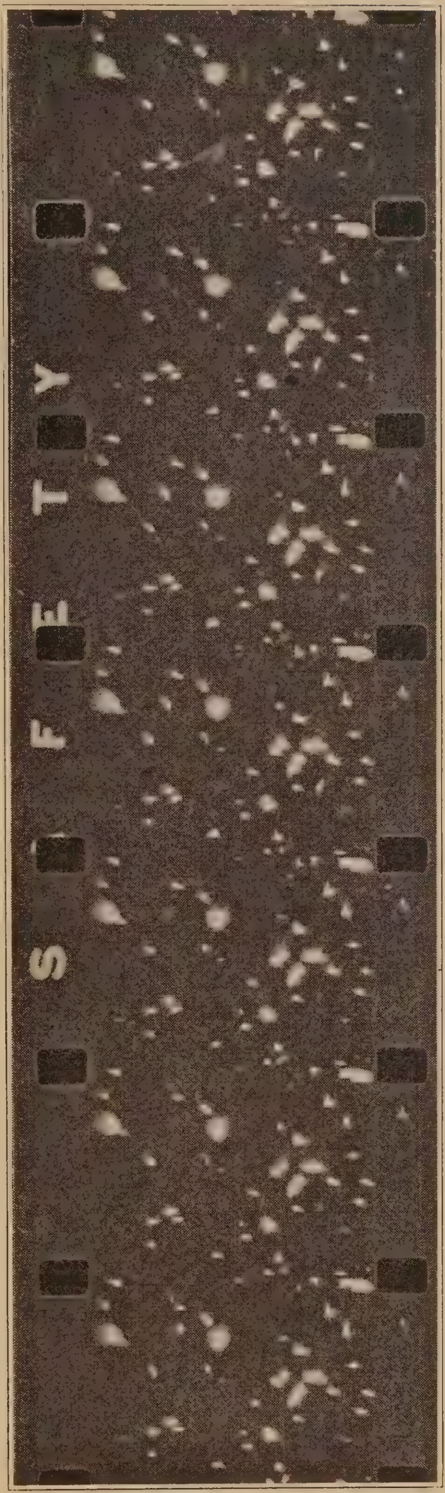

FIG. 4.—English china clay (alkaline).

which apparently afford a means of determining their relative order of plasticity. This would seem to indicate that there is some foundation for the numerous statements found in the literature claiming a relation between plasticity and colloidal content. However, before drawing any

FIG. 5.—English china clay (acid).

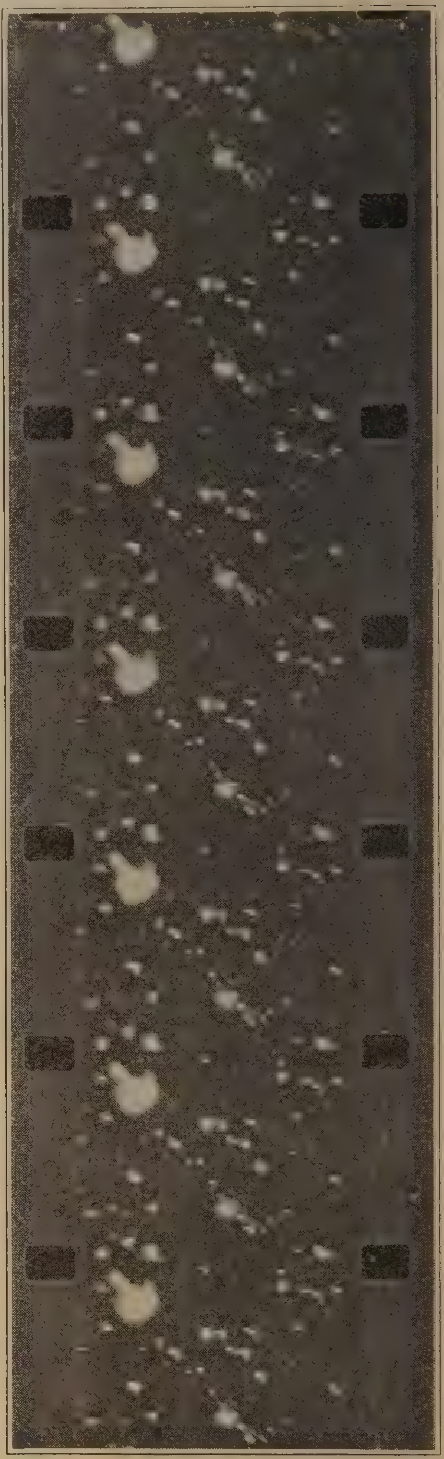

FIG. 6.—South Carolina kaolin.

definite conclusions in this connection, the present work should be extended so as to include a wide variety of clays of definitely known plasticity. Furthermore, in order to prevent the possibility of including particles exceeding ultramicroscopic dimensions, the colloidal fractions should be collected by means of a high speed centrifuge. Valuable

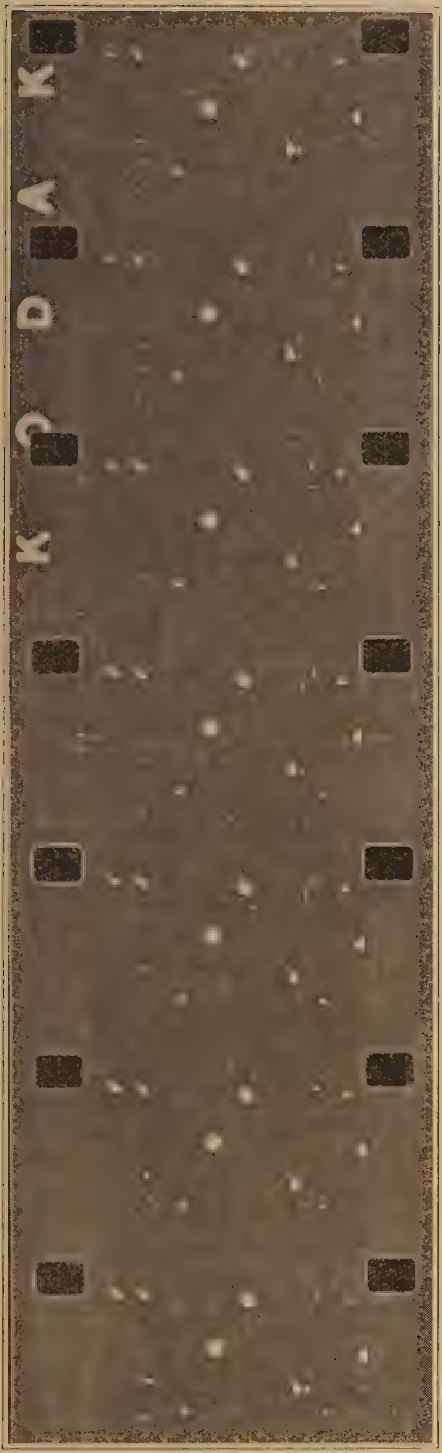

Fig. 7.—North Carolina kaolin.

Fig. 8.—Fireclay semi-flint.

information, as indicated by Figs. 4 and 5, could also be obtained from a systematic study of the flocculation and deflocculation effects of electrolytes by means of the ultramicroscopic motion picture method. These and similar problems are now in progress in this laboratory.

Conclusions

1. Attention has been called to the confusion in the use of the term "colloid."

2. A simple and convenient ultramicroscopic motion picture method, employing comparatively inexpensive and readily procurable equipment, for the study of colloidal systems has been described.

3. Characteristic differences have been shown to exist in the colloidal fractions of clays of different plasticities.

4. The relative order of plasticity of four clays has been determined by these differences.

5. Some evidence has been obtained in support of the belief that a relation exists between the plasticity and the colloidal content of a clay.

The writer expresses his thanks to Julius F. Stone through whose generosity the ultramicroscope and motion picture equipment used in this work were provided.

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THE MINERALS OF BENTONITE AND RELATED CLAYS AND THEIR PHYSICAL PROPERTIES[1]

By Clarence S. Ross and Earl V. Shannon

ABSTRACT

Bentonite is a very widely distributed clay material that is the result of the devitrification and chemical alteration of glassy volcanic ash or tuff. Bentonite should be used as the name of a rock derived from volcanic glass and it is commonly composed of the mineral montmorillonite but less often of beidellite. Its characteristic minerals are completely crystalline and have a micaceous habit, high birefringence and facile cleavage. It contains no gel colloids, and few of its crystal particles are so small as to reach "colloidal size." It shows high adsorptive powers and this property is more dependent upon physical form than upon chemical composition. That is upon the micaceous structure and easy cleavage which give very great surface area and the felt-like texture which facilitates permeability.

The clay minerals of the type here described resemble the micas in many ways, but do not seem to possess the marked chemical variability of that group. A large number of analyses of the clay minerals from bentonite indicates that the most widespread of these is montmorillonite with the formula $(Mg, Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$.

A reanalysis of the type montmorillonite from Montmorillon, France, gives the same formula, and the mineral has also been recognized in lithium-bearing pegmatites and in fullers' earth.

A few bentonites are composed of beidellite, a mineral first identified from the gouge clay of ore veins. It has the formula $Al_2O_3 \cdot 3SiO_2 \cdot nH_2O$ where n = about 4, and Al_2O_3 may be partly replaced by Fe_2O_3.

A third micaceous clay mineral has the composition of halloysite $Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$, but it is completely and visibly crystalline and has a high birefringence.

Introduction

Clays are fundamentally minerals or aggregates of several minerals and yet, notwithstanding their universal occurrence and great industrial importance, less is known of them than of any of the widely occurring minerals. Their investigation has been delayed by the fact that they are often composed of complex aggregates of minerals of very fine-grained or amorphous texture, but there is no reason for believing that careful and systematic study by modern research methods will not bring them within the realm of organized knowledge. This situation has led the writers to undertake a thorough study of one group of clay minerals with three main objects in view. The first and most important has been to determine whether the clay minerals can be studied and explained by the methods now at the disposal of the mineralogist. The second has been to extend the knowledge of an important mineral group, and the third has been to point the way and perhaps inspire other workers to extend the investigation to include all the clay minerals.

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[1] Printed by permission of the Director of the United States Geological Survey and the Secretary of the National Museum. Recd. Dec. 3, 1925.

For these reasons the minerals of bentonites and related clays have been under investigation in the laboratories of the U. S. Geological Survey and the National Museum for the past two years. The work has had many ramifications; alluring avenues of research have led even into complex problems about the constitution of matter; and results have been attained that throw light on many mineralogical problems.

The clays that have been included in this study are those characteristic of bentonites, the gouge clays of ore veins and the related minerals from altered pegmatites. These are not clays that are extensively used in the ceramic industries but they are pure minerals or are capable of being purified and so constitute a point of departure in a study of clay minerals. They occur with less purity in shales, soils, and even in metamorphic rocks and appear to be more widely distributed than kaolinite which has often been considered the characteristic clay mineral.

The characteristic mineral from twenty bentonites and related clays has been analyzed, and often very careful purification and optical study has been necessary to assure the purity of the material. Over 300 thin sections have been made and examined, and to do this it has been necessary to develop an entirely new technique for grinding thin sections. The new methods make it possible to grind thin sections without the customary use of water and to retain perfectly the original texture no matter how delicate or friable the clay may be. The optical properties have been determined on hundreds of specimens, where the individual mineral grains are usually exceedingly fine grained. This exhaustive work still leaves many problems unsolved, but it is believed that distinct progress has been made and some firm ground has been reached.

The present paper is a condensed statement of the results and deductions that will be of most interest to ceramists, but it is planned to publish the complete results later, either through the U. S. Geological Survey or the National Museum. The study of clays composed of pure minerals with definite properties provides a new approach to the problem of the causes of plasticity in clays, and a paper on the subject is under preparation and will follow this one.

Bentonite

Bentonite has peculiar and perhaps valuable properties that have aroused much interest and speculation, but there has been little agreement as to the physical or chemical nature of the material and no careful investigation of its properties. The present work has shown that bentonite is composed of a definite mineral which can be studied by the same methods that have been applied to other minerals, and its peculiar properties can be explained on the basis of the ascertained properties of its individual crystal grains. Thus bentonite is completely amenable to the research methods of mineralogy and geology.

The following definition of bentonite is proposed:

Bentonite is a *rock* composed essentially of a crystalline clay-like mineral formed by devitrification and the accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash; and it often contains variable proportions of accessory crystal grains that were originally phenocrysts in the volcanic glass. These are feldspar (commonly orthoclase and oligoclase), biotite, quartz, pyroxenes, zircon and various other minerals typical of volcanic rocks. The characteristic clay-like mineral has a micaceous habit and facile cleavage, high birefringence and a texture inherited from volcanic tuff or ash, and it is usually the mineral montmorillonite, but less often beidellite.[1]

It is advisable to restrict the rock name bentonite to a material derived from volcanic ash, since the inherited structure seems to have almost as great an influence on the physical properties as the mineral composition. It is quite evident that a mineral with the same chemical composition as that found in bentonite can develop in other ways. Thus the mineral that is often found in lithium-bearing pegmatites is undoubtedly montmorillonite and at least some fullers' earth has the same composition, but their origin and texture are different and so they would not be called bentonite. Beidellite, which occurs in some bentonite, is also found in gouge clays that are very different from bentonite.

Bentonites often contain detrital material from various sources in addition to the igneous rock phenocrysts, and sands may be mixed with bentonitic material in all proportions. It is probably best to confine the name bentonite to material with at least 75% of the bentonitic clay minerals and less than 25% of sandlike or other impurities. If it contains between 25 and 75% of sandy impurities it may be called an arkosic bentonite and with less than 25% of the bentonitic clay minerals it may be called a bentonitic arkose. Shales may also contain admixed bentonitic material, but in these its certain identification is very difficult or even quite impossible.

Occurrence of Bentonite

Bentonite has been reported from every state west of the Missouri River and from Kansas, Oklahoma, Texas, Louisiana, Arkansas,

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[1] Esper S. Larsen, and Edgar T. Wherry, *Jour. Wash. Acad. Sci.* **15,** 465 (1925).

Tennessee, Alabama, Virginia, Kentucky, Pennsylvania, Minnesota, Wisconsin, and probably other eastern states. It is found in Old Mexico, in much of western Canada, Alaska to beyond the Arctic Circle, in China, and possibly in France. It has been found in the Paleozoic and Mesozoic beds, but is probably most abundant in the Tertiary.

The distribution, uses, physical properties, and bibliography of bentonite are admirably given by Hugh S. Spence[1] in a recent *Bulletin* of the Canada Department of Mines. A large number of analyses are quoted, but these represent the crude samples and are not intended as a study of the composition of the characteristic clay mineral of bentonite.

Volcanic debris has contributed material to the sedimentary beds over wide areas in the western states and these frequently contain much bentonitic material. Renick[2] has shown that this more or less sparsely disseminated bentonitic material may have an important bearing on the chemical composition of ground waters.

Habit and Structure

Bentonite is an extremely variable material in its outward appearance and superficial physical properties. The most widespread color is probably pale buff, cream or dull green, but gray, dull blue, green and pink are not uncommon. Less frequent colors are deep olive green, red, and yellow. Some specimens are nearly white when dry, but pure white is not often seen in bentonites. However, one known deposit yields material that is pure white even after wetting.

Some bentonites are very compact in texture and have a sharp conchoidal fracture. Others are more open and porous, and some have a very loose feltlike texture. After the bentonite was formed, its texture has often been modified by the deposition of material that was carried in solution. Small bead-like grains of calcium or iron carbonate are often seen, and in some deposits calcium carbonate has completely filled the pores and produced a dense hard rock. Small black spots of manganese oxide are found in some deposits and gypsum and barite crystals are abundant in others. Alkalis and alkali salts occur in varying amounts and this rôle will be more fully discussed in page 89.

The study of thin sections of bentonite reveals two outstanding features: (1) that bentonite is derived from volcanic ash, as has been pointed out by Hewett[3] and Wherry,[4] and (2) that its characteristic

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[1] Hugh S. Spence, Can. Dept. Mines. Mines Branch.

[2] B. Coleman Renick, "Base Exchange in Ground Water by Silicates as Illustrated in Montana," U. S. Geol. Survey, *Water Supply Paper* **520-D,** 53–72 (1924).

[3] D. F. Hewett, "The Origin of Bentonite," *Jour. Wash. Acad. Sci.*, **7,** 196–98 (1917).

[4] E. T. Wherry, "Clay Derived from Volcanic Dust in the Pierre of South Dakota," *Jour. Wash. Acad. Sci.*, **7,** 576–83 (1917).

mineral is definitely crystalline. The ash structure is perfectly preserved in a large proportion of the sections. Devitrified glass bubbles are sometimes seen; the segments of hollow spheres, the angular or Y-shaped or lune-shaped fragments that result from the fracture of rounded bubbles or groups of bubbles are a widespread type; the flattened plates that are derived from elongated and lens-shaped bubbles are probably most abundant; and pumice fragments with a fibrous habit are not rare.

Thus all the types of structure that occur in glassy volcanic ash[1] are represented in bentonite.

The microscopic examination between crossed nicols of the petrographic microscope shows that the characteristic mineral of bentonite is crystalline, as has long been maintained by Larsen,[2] Wherry,[3] and others. In some specimens the material is very fine-grained but in most of them the crystal grains can be seen even with low magnifications. The mineral has a micaceous habit, and moderately high birefringence perpendicular to the cleavage. The groups of plates that have been derived from a single glass fragment commonly have a definite arrangement, and sharply outline the original fragment. In most types of bentonite the crystal plates stand perpendicular to the original surface of the glass fragment, and the resulting crystalline area is now composed of two parallel rows of micaceous plates that often have a parting line between them. In other specimens the micaceous plates have developed parallel to the sides of the glass. Crystalline areas of these two types appear to show a positive and negative character of elongation but the anomaly is usually explained on an examination with an oil immersion lens which shows the real orientation of the plates. In a few bentonites both orientations are to be seen, and a laminated structure has been observed with two outer rows of plates lying perpendicular to the surface, and separated by a film in which the plates lie parallel to the length of the fragment.

Figures 1 and 2 show photomicrographs of several types of bentonite. All were taken under crossed nicols and the light-colored areas are definite evidence of the crystalline nature of the grains, for no light is transmitted through the upper nicol by noncrystalline material. The high birefringence shows only when the micaceous plates stand perpendicular to the thin section and plates that lie nearly parallel are black or dark gray. The magnification is low in all the sections and so the comparatively large size of many of the individual crystal areas is evident. Thus the large platelike fragment of uniform crystal structure in *a*, Fig. 1, is nearly 3 millimeters in length and the larger plates in *a*, Fig. 2, are equally large.

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[1] L. V. Pirrson, *Amer. Jour. Sci.*, **40** [4], 193 (1915).

[2] E. S. Larsen, Personal communication to Hugh S. Spence in *Bull.* **626**, of the Mines Branch, Dept. of Mines, Canada, 1924.

[3] Edgar T. Wherry, *Jour. Mineralogical Soc. of Am.*, **10**, 65 (1925).

An unusually perfect devitrified glass bubble is shown just to the right of the middle in *a*, Fig. 1.

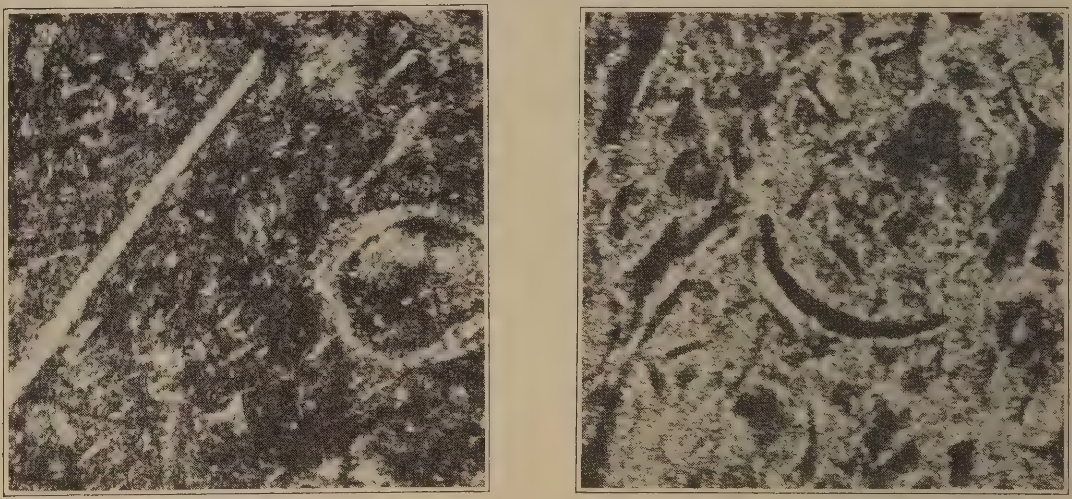

FIG. 1*a* FIG. 1*b*

FIG. 1.—(*a*) Bentonite. Encinitas, San Diego Co., Calif. Rounded, unbroken bubble wall and platy tuff fragments. Crossed nicols. Magnification 20 ×.

(*b*) Bentonite. Dome, Arizona. Gray areas bentonite ground-mass, black residual bubble walls of unaltered glass. Crossed nicols. Magnification 10 ×.

Bentonites with incompletely devitrified glass are not common but a very good example is shown in *b*, Fig. 1. The black areas are isotropic glass and the lighter areas are made up of rather finely granular crystalline material. *a*, Fig. 2, is made up almost exclusively of platy fragments that have altered to very sharply bounded crystalline areas.

b, Fig. 2, is part of a fragment that was originally 6 to 8 decimeters in diameter which came from a coarse tuff. It shows very perfectly the flow structure that is characteristic of many glassy volcanic rocks. All these textures have been retained in a material that is now clay, and yet the volcanic rock structures are as perfect as they could have been on the day that the original glass cooled. The perfection with which structures have been retained is one of the remarkable features of bentonite.

The bentonites that have been derived from a platy volcanic ash commonly show an orientation of the plates parallel to the bedding. There appears to be a loss of volume on alteration from glass to the clay-like material, and the deposit certainly becomes more compact.

During the process the individual fragments become slightly plastic and assume a somewhat crenulated form as they accommodate themselves to the shape of their neighbors. The loss of volume and degree of compacting can not be excessive, however, for the rounded forms of glass bubbles are often practically unmodified by flattening.

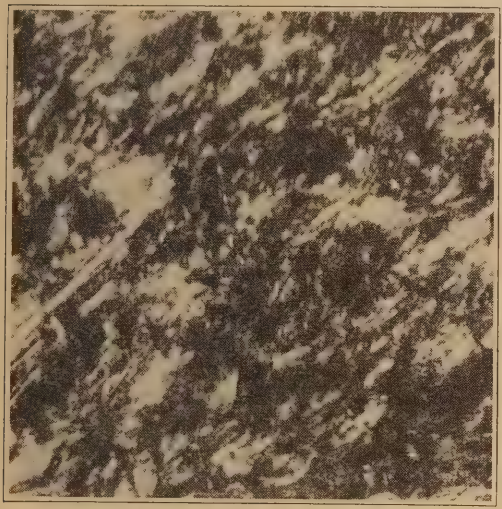

FIG. 2*a*

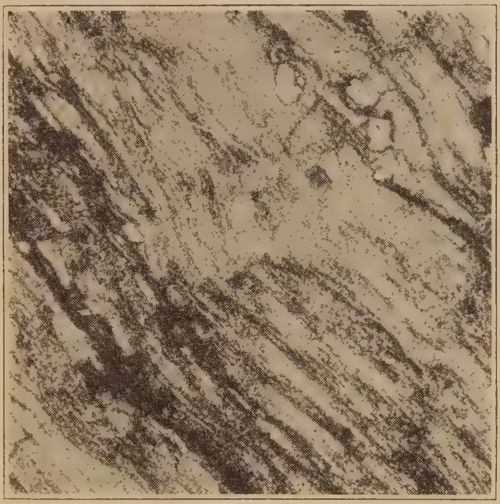

FIG. 2*b*

FIG. 2.—(*a*) Bentonite. Brown property, Nevada. Platy volcanic ash fragments. Crossed nicols. Magnification 10 ×.

(*b*) Rideout, Utah, fragment of volcanic flow rock altered to bentonite. Small rounded areas are feldspar. Crossed nicols. Magnification 20 ×.

The conspicuous and often coarsely crystalline texture of bentonite precludes a purely "colloidal" explanation of its physical properties. Bentonite has long been a favorite theme for those who believe that adsorptive properties are inseparably associated with colloids, and it has been one more substance for which the colloidal theory has been invoked. Thus the literature is full of references to it as a "colloid" or as a "typical colloid." Any material can be dispersed till its particles reach dimensions that have been termed colloidal, and variable proportions of bentonite no doubt reach this arbitrary degree of dispersion. A large proportion of the crystalline grains can be observed with moderate magnifications in a slurry made from most bentonites, and the proportion of large discrete mineral grains is far greater in the undisturbed dry bentonite. However, if those assuming the "colloidal" nature of bentonite clearly recognized that it was a finely divided crystalline material as are most colloids,[1] the difference of view would not be great for then there would be only a question of the degree of dispersion. However, there appears to be a fatal tendency to forget all about crystalline dispersoids and to think of so-called colloids in terms of amorphous gels which have been defined as a coagulated liquid-liquid system. Thus many have reasoned on the basis of its adsorptive properties that bentonite was a colloid and then assumed that it was an amorphous gel, all unmindful that direct observation is the first step in research. Bentonite does show very great adsorptive powers but this is the result of the physical structure that gives great surface area and is due only in a minor degree to the small size of the individual crystal grains.

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[1] Svedberg, *Chem. Rev.*, **1** [3], 629 (1924).

The minerals that are associated with the clay-like devitrification products of glass and that represent igneous rock phenocrysts are orthoclase, plagioclase, biotite and augite and less often hornblende, muscovite, zircon, apatite, etc.

Quartz that was clearly an essential mineral in the original rock is present in some bentonites, although usually in rather limited amount, but it is entirely absent in others. Bentonite also contains quartz of detrital origin, that evidently became mixed with ash that fell upon land and was later reworked before deposition in the sea.

The alteration of the glassy igneous material into bentonite is so complete that it is usually possible to arrive at the original composition only by inference. Feldspar (usually orthoclase) is the predominant phenocryst and is often the only one present, and biotite is not rare. Thus the phenocrysts are generally those that are characteristic of quartz-free trachytes, latites, quartz latites, and possibly quartz-poor rhyolites but seldom quartz-rich rhyolites. Trachyte and latite are composed of silicate minerals with the highest possible silica ratio and rhyolite is composed of the same type of silicates plus quartz, and it is to be noted that these rocks so far as known give rise to bentonites that are composed of montmorillonite, the clay mineral with an alumina-silica ratio of 1 to 5.

The arkosic bentonite of southwestern Arkansas is composed of the clay mineral represented by analysis 21, page 94, and is the result of the alteration of nephelite-bearing rocks. The iron-rich bentonitic clay represented by analysis 25, page 94, is the result of alteration of an olivine basalt. Both these bentonites are characterized by the beidellite type of clay mineral with an alumina-silica ratio of 1 to 3, and both are derived from rocks with a deficiency of silica. The evidence at hand does not permit broad generalizations, but it seems quite probable that glasses very high in silica are fairly stable and do not readily alter to bentonite. The silica content above which a glass is not likely to alter to bentonite is perhaps about 68 or 70% SiO_2, although the limit is probably far from definite. Glasses with an intermediate silica content that approach a feldspar glass in composition alter to montmorillonite with a 1 to 5 ratio of alumina to silica and those low in silica alter to beidellite with a 1 to 3 ratio.

The conditions that favor the change from glass to bentonite are not well known. Many bentonites occur in marine sediments, but others are in non-marine beds, although the possibility that the ash fell in saline lakes cannot always be excluded. The process of alteration is largely one of hydration accompanied by devitrification and leaching out of alkalis and possibly of other bases. It may be that bentonite is merely the result of the instability of glass of a certain composition in the presence of water and the salts that are normally dissolved in it, and that no unusual conditions are required for its formation. The wide distribution of bentonite also suggests that its formation is not dependent upon special conditions.

Other workers on the subject have come to the conclusion that the active gases that are abundant in volcanoes of the explosive type have played a part in the production of bentonite by initiating the alteration that was completed after the deposition of the ash.

The great purity of many bentonites, and the preservation of delicate structures like bubble walls and glass shreds, show that the ash from which it was derived must have been deposited directly from the air. The wide extent of those deposits and their distance from a known volcanic source emphasize the stupendous proportions of some of the volcanic eruptions of the past.

Some bentonites contain much non-volcanic detrital material and have lost the characteristic ash structure. This type probably first fell upon land and was later reworked and redeposited like other detrital sediments. Sometimes only the upper part of the bed is reworked and this is probably the result of wave action in shallow water.

Different bentonites have quite different physical properties. Most of them swell slightly and crumble in water, but do not become plastic. Most of them contain little material that remains in suspension more than a few hours, even after having been agitated in water for many hours. A few become plastic, swell greatly, and a large proportion of the material may remain in permanent suspension. This difference is partly due to variations in structure, and possibly in part to natural salts that act as flocculating and deflocculating agents. The swelling is primarily due to the micaceous habit and the very slight cohesion between crystal plates, so that films of water penetrate between them. Thus on wetting and slaking, the crystalline aggregate that makes up the bentonite, subdivides into micaceous plates that have large lateral extent but many of them probably have a thickness that is best expressed in molecular dimensions.

Wherry[1] has suggested the term "one dimensional" colloid for the very thin micaceous plates of dispersed bentonite which he says "exhibit optical and physical properties which indicate that their grains are of visible dimensions in two-space directions, but submicroscopic and colloidal in the third, perpendicular to the micalike plates." This peculiar micaceous habit and the easy cleavage, which is only potential in the original bentonite, but that may become actual in a slurry, results in a material that has tremendous surface area ready to exert adsorptive powers, and gives the greatest possible ratio between area and mass. The open felted texture allows water to quickly penetrate throughout the mass so that the entire surface area of the micaceous plates is quickly covered by a film of water. This happy combination of large surface area and permeable texture gives bentonite the greatest efficiency for adsorption that nature ever seems to have devised.

Mineralogy of Bentonite and Related Clays

Most bentonites are composed of the clay mineral montmorillonite, but a few are characterized by the related mineral beidellite. Montmorillonite has also been identified from altered lithium-bearing pegmatites, beidellite from gouge clays in mineral veins, and a micaceous mineral that has the composition of halloysite from altered pegmatites and gouge clays. These minerals have different chemical compositions but resemble each other in being obviously crystalline and often rather coarsely crystalline; in possessing a platy, or micaceous habit and easy cleavage, and rather high birefringence. They resemble the micas in many ways and may sometimes be mistaken for them, and they differ in many ways from kaolinite and halloysite. Beidellite and the micaceous mineral corresponding to halloysite have somewhat higher indices of refraction and higher birefringence than montmorillonite but all are characterized by a high water content. They all possess marked adsorptive powers which appear to be more dependent upon physical form than chemical composition. Beidellite and montmorillonite have heretofore been grouped with leverrierite and the other mineral has not been differentiated from halloysite. Leverrierite is imperfectly known and its place in the group is undertermined.

Chemical Composition

The crystalline clay minerals, despite their fineness of grain, are characterized by platy structure and eminent basal cleavage and have many of the physical properties of the mica division, which includes the true micas and chlorites as well as many poorly known highly hydrous silicates generally called hydromicas and vermiculites. Many of these are among the most difficult of all minerals to interpret chemically and even the best analyses made upon well-crystallized and pure material show wide variations in composition even though classified as a single mineral. Several complex theories have been put forward to explain the chemical constitution and account for the variation but none of these seems entirely satisfactory.

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[1] Edgar T. Wherry, *Jour. Mineralogical Soc. of Amer.*, **10**, 65 (1925).

The clay minerals, being micaceous, might be expected to exhibit all the vagaries of composition found in the more coarsely crystallized micaceous minerals. The study of bentonite and some other related clays has, however, given results which apparently indicate that the clay minerals are few in number and that each is a single definite chemical compound of simple type rather than an isomorphous mixture of two or more dissimilar end-members. The pure clays that have been studied are composed of one of the following five distinct clay minerals. Two of these have been found in the bentonites and the other three have been encountered in non-bentonitic clays. These five minerals may be enumerated as follows:

Name	Chemical Composition	Physical form	Crystal system
1. Montmorillonite	$(Mg,Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$	micaceous	orthohombic?
2. Beidellite	$Al_2O_3 \cdot 3SiO_2 \cdot nH_2O$	micaceous	orthohombic?
3. Micaceous halloysite	$Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$	micaceous	orthohombic?
4. Halloysite	$Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$	amorphous or submicroscopical crystalline	unknown
5. Kaolinite	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	platy crystalline	monoclinic

The analyses of bentonite hitherto published showed great variations in composition, particularly in the ratio of alumina to silica. In part this seemed to be the result of poor analytical work but it was apparently largely due to the presence of detrital grains of foreign material which were not removed from the samples prior to analysis. The purest and cleanest bentonites showed a distinct similarity to each other in composition and approached the clay mineral montmorillonite. They differed from the original analyses of montmorillonite, however, in the almost invariable presence of more or less of bivalent bases, notably magnesia with less lime. The analyses by the present writers were all made upon carefully selected or purified material. The method of purification consisted in thoroughly disintegrating the clay in water and decanting the material which remained in suspension various lengths of time. In this manner the clay substance could be rather uniformly graded and several crops of clay grains secured that were practically free from the impurities, which settled to the bottom of the vessel together with the coarser particles of the clay mineral. This method can be applied to bentonites for the impurities are igneous rock phenocrysts that are larger and more uniform than the impurities in residual or detrital clays. In several cases coarser and finer samples obtained from the same clay were analyzed separately and it was found that, when free from foreign materials, these did not differ appreciably from each other in composition.

The majority of the bentonite analyses made upon pure material agreed with each other in giving a formula similar to that for montmorillonite but slightly higher in silica ratio and containing approximately one molecule of bivalent bases. A portion of the type material of montmorillonite from Montmorillon, France, was obtained for comparison by exchange from Prof. Lacroix of Paris. This was reanalyzed and found to give results closely comparable with those of the American bentonites. The French montmorillonite does not show a definite volcanic ash structure and it probably is not bentonitic. Montmorillonite can, however, form by other processes than those producing bentonite. Wells[1] has analyzed a montmorillonite occurring as an alteration product of spodumene in pegmatite at Branchville, Conn., and the present writers have examined a clay of similar origin from Embudo, New Mexico, which also proved to be montmorillonite.

In the following there are presented a selection of analyses of bentonites:

Table I

Analyses of Bentonite (Montmorillonite)

	1	2	3	4	5	6	7
SiO_2	51.10	48.80	50.30	49.56	51.56	54.46	57.28
TiO_2	——	——	——	.40	.78	.80	.50
Al_2O_3	15.40	21.08	15.96	15.08	13.42	16.84	16.04
Fe_2O_3	4.50	.92	.86	3.44	3.22	3.36	4.02
MnO	——	——	——	.01	——	——	——
CaO	5.20	1.36	1.24	1.08	2.04	3.20	1.72
MgO	3.80	4.84	6.53	7.84	4.94	4.84	3.28
K_2O	1.50	——	.45	——	.38	——	——
Na_2O		——	1.19	——	.24	——	——
H_2O	17.10	20.92	23.61	22.96	23.46	16.10	17.10
Total	98.50	97.92	100.24	100.37	100.04	99.60	99.94

1. Bentonite, selected crude, Ardmore, S. Dak. Anal. by E. T. Wherry, *Jour. Wash. Acad. Sci.*, **7,** 580 (1917).
2. Bentonite, Ardmore, S. Dak. Fine portion. Purified by Clarence S. Ross, Earl V. Shannon, analyst.
3. Bentonite (otaylite) crude selected white material, near Otay, San Diego Co Calif. J. E. Whitfield, analyst.

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[1] H. L. Wells, *Amer. Jour. Sci.*, **20,** 283 (1880).

4. Bentonite (otaylite) crude selected pink material, near Otay, San Diego Co., Calif. Earl V. Shannon, analyst.
5. Bentonite, pink friable matrix of bentonite tuff. Three miles north of the east end of the Tierra Amarilla Grant, New Mexico. Purified by Clarence S. Ross. Earl V. Shannon, analyst.
6. Bentonite, pink friable matrix of bentonite tuff. Conejos Quadrangle, Colorado. Separated and purified by Clarence S. Ross. Earl V. Shannon, analyst.
7. Bentonite. Sent from Boise, Idaho, by Edward Schwerd. Contained abundant calcite which was removed with dilute hydrochloric acid. Earl V. Shannon, analyst.

TABLE I (*continued*)

ANALYSES OF BENTONITE (MONTMORILLONITE)

	8	9	10	11	12
SiO_2	50.33	49.20	52.08	56.20	50.28
Al_2O_3	16.42	17.60	18.20	13.20	20.00
Fe_2O_3	2.42	1.60	2.88	5.08	4.00
CaO	1.39	1.52	2.28	1.60	1.08
MgO	4.10	5.08	4.48	2.92	4.60
K_2O	1.00	——	——	——	——
Na_2O	.12	——	——	——	——
H_2O	23.95	25.52	20.80	20.32	19.60
Total	99.85	100.52	100.72	99.32	99.56

8. Bentonite. Sent in by G. A. Martin of Maricopa, Kern County, Calif. Selected crude. Earl V. Shannon, analyst.
9. Bentonite. Fort Steele, Wyoming. Purified by Clarence S. Ross. Earl V. Shannon, analyst.
10. Bentonite. Wisconsin, Texas. Purified by Clarence S. Ross. Earl V. Shannon, analyst.
11. Bentonite. Quilchena, B. C. Furnished by Hugh Spence, of Mines Branch Geol. Survey of Canada. Purified by Clarence S. Ross.
12. Bentonite. Sent in by California Master Products Corp., of Los Angeles, Calif. Purified by Clarence S. Ross. Earl V. Shannon, analyst.

For purposes of comparison the analyses of montmorillonite of non-bentonitic origin are given in Table II. The agreement between the analyses of the bentonites is remarkably good especially when it is borne in mind that the materials are of detrital origin, are exceedingly fine-grained and high in absorptive and adsorptive capacity. The presence in approximately constant amount of bivalent bases, principally magnesia with less lime, has led to the conclusion that these are an essential part of the mineral molecule. Consequently the present writers have written the formula for this mineral

$$R''O \cdot R'''_2O_3 \cdot 5SiO_2 \cdot 5\text{–}7H_2O$$

Where the bivalent bases fail in a few cases the similarity can still be expressed by writing one molecule of water, basic and replaceable thus:

$$(H_2, Mg, Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot 5\text{–}7H_2O$$

Heretofore it has been customary to consider the magnesia and lime present in these clays to be adsorbed or present as extraneous impurities but this interpretation seems no longer tenable.

The analyses given in Tables I and II seem to show conclusively that the clay mineral of these bentonites is identical with montmorillonite and they clearly support the formula here proposed. The Attapulgus, Georgia, fullers' earth likewise conforms with this formula and it is interesting to draw attention to the fact that the formula derived by Fersman[1] for a Russian fullers' earth is the same.

Table II

Composition of Montmorillonite

	13	14	15	16	17	18
SiO_2	49.40	48.60	51.20	48.24	51.28	50.60
Al_2O_3	19.70	20.03	22.14	22.32	10.56	17.23
Fe_2O_3	.80	1.25	——	.36	6.76	——
CaO	1.50	1.72	3.72	2.04	1.44	3.21
MgO	.27	5.24	3.53	6.64	10.40	4.56
MnO	——	.16	.18	——	——	——
$(K, Na)_2O$	1.50	——	.56	——	——	——
H_2O	25.67	21.52	17.08	20.84	20.28	24.32
P_2O_5	——	——	1.42	——	——	——
Total	98.84	98.52	99.83	100.54	100.72	100.00

13. Montmorillonite, Montmorillon, France. Analysis by Salvetat; Dana System of Mineralogy, p. 690.
14. Montmorillonite, Montmorillon, France. Earl V. Shannon, analyst.
15. Montmorillonite from pegmatite, Branchville, Conn. H. L. Wells, analyst. Dana System of Mineralogy, p. 690.
16. Montmorillonite from pegmatite, Embudo, New Mexico. Collected by F. L. Hess. Earl V. Shannon, analyst.
17. Fullers' earth, Attapulgus, Georgia. Purified by Clarence S. Ross. Earl V. Shannon, analyst.
18. Montmorillonite. Theoretical composition to satisfy the formula $(Mg, Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot 8H_2O$, with MgO : CaO present in the ratio of 2 to 1.

The analyses in the two preceding tables show some variation, but it will be seen that, aside from minor deviations, the proportions of bivalent bases, silica, and trivalent bases, alumina plus ferric iron, is decidedly constant. The essential constituent of greatest variability is the water which, while always large in amount, varies from 16.10% to 25.67%. The behavior of the water content of this mineral is of especial interest and has given basis for some very instructive speculation as to the manner in which the moisture is held or combined. The above analyses were in all cases made on air-dried material, that is, material which had been exposed in powdered form to the room or laboratory atmosphere until all of the excess moisture had dried off. The amount of water held by a given sample varies with the temperature and humidity of the surrounding atmosphere so that the same sample shows very appreciable differences in the amount of water when analyzed on different days if there is much difference in the relative humidity. A large part of the water is driven off at a temperature of 120°C, and much is lost at room temperatures in a dessicator over sulphuric acid and calcium chloride. Samples which have been dried to constant weight at 120° or possibly somewhat higher and have lost upwards of 12% of moisture, regain this in a few hours when allowed to stand exposed to the air of the room. The temperature of 110°C is without any significance whatever in the dehydration of these materials and, when the temperature is increased a few degrees, samples which have been brought to constant weight, lose additional water. The behavior of this water has not been fully investigated and more detailed study is planned. The behavior of two samples is tabulated below:

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[1] A. E. Fersman, *Revue de Geologic*, **5**, 98 (1919).

LOSS OF WATER BY MONTMORILLONITE CLAYS

	1 Montmorillonite (France)	2 Otaylite (California)
100°C	11.88%	14.28%
140°C	2.00	1.48
450°C	2.64	2.44
Red heat	5.00	4.76
Total	21.52	22.96

The clays were heated until they had reached constant weight at each temperature. When samples which had been brought to constant weight at 140° were allowed to stand overnight in air they gave the following results:

	1 Montmorillonite (France)	2 Otaylite (California)
Lost at 140°	13.88	15.76
Regained overnight	13.88	11.56

This large amount of water which is so easily lost and regained seems to be without visible effect upon the optical properties of the mineral. From the above table it will be seen that only 5% or less of water is held by the mineral above 450°. This is a distinct difference from kaolin, halloysite, and the other clay tabulated above with the composition of halloysite, all of which retain water molecularly equivalent to the silica to a red heat.

The water content is subject to such variation under varying conditions that the exact statement of it in the formula is not practicable. The variation seems to be at least from 5 to 8 H_2O in the formula given for montmorillonite. The behavior of the water, the ease with which it is lost and regained and the fact that the physical properties of the mineral are not changed by the driving off of a large part of the water, has led the writers to the conclusion that this water is in large part adsorbed and not an essential integral part of the chemical molecule making up the mineral. This tendency to adsorb such large amounts of water is doubtless a function of the physical structure of the material which, being extremely finely micaceous gives relatively enormous surface area. This is one of the so-called colloidal properties which has led to bentonite being considered a colloid.

Two clays of bentonitic habit and appearance which were examined were found to have the same alumina-silica ratio and about the same amount of bivalent bases as the above but they differed in the presence of nearly 6% of potash and in having very considerably less water than the average under the same conditions. The analyses of these are given below as Table III:

Table III

Analyses of Potash Bearing Bentonites

	19	20
SiO_2	55.64	53.12
Al_2O_3	16.80	18.72
Fe_2O_3	2.68	1.12
CaO	1.80	1.40
MgO	8.88	6.92
K_2O	5.16	5.72
Na_2O	.04	trace
H_2O	9.72	12.04
Total	98.72	99.04

19. Bentonite, "soap clay" from Suifu, China. Collected by D. C. Graham, purified by Clarence S. Ross. Analyzed by E. V. Shannon.
20. Bentonite. High Bridge, Kentucky. Coll. Charles Butts. Purified by Clarence S. Ross, Analyzed by Earl V. Shannon.

These clays with their high potash and low water contents introduce a very interesting question of the relationship of water to potash. The variation of the water from day to day is shown above in comparison with typical montmorillonite. Aside from the potash content both of these agree reasonably well with the chemical formula given for montmorillonite. The potash, figured out to molecular ratio, is not sufficient in amount to deserve place in the formula. The most striking thing about the presence of the potash is that total water varies inversely with the alkalis, one weight per cent of potash being approximately equal to two weight per cent of water. This ratio seems to hold good also for examples of these clays which contain smaller amounts of alkalis. This ratio bears no relation to the molecular weights of water and potash. It seems most reasonable to conclude that the potash, like the major part of the water, is adsorbed. Furthermore it appears that one part of adsorbed potash displaces approximately two parts of adsorbed water. The potash could not be extracted from the Kentucky material with hydrochloric acid.

Selective adsorption of potash without corresponding adsorption of soda has been recognized as a property of soils for some time but the adsorption was credited to the "soil colloid." Chemists interested in the search for a commercial potash supply in this country were long puzzled to account for the almost total absence of potash from the salt deposits of the closed desert basins. It was obvious that potash had been delivered to these basins in amount equal to or greater than the soda. It finally became apparent that the potash had been adsorbed by the muds whereas the soda had remained in the solutions. To this selective adsorption of potash by clays having "colloidal" adsorptive properties can be credited the fact that the ocean is salty from sodium chloride rather than a mixture of the chlorides of sodium and potassium.

Beidellite

A single occurrence of clay of unquestionably bentonitic structure and origin failed signally to show an agreement with the others, both in alumina to silica ratio and in the relative amount of bivalent bases. This clay, from Mine Creek near Nashville, Howard County, Arkansas, cannot be identified with montmorillonite although having many physical properties in common with that mineral. It does agree, however, with certain gouge clays which have been called leverrierite,[1] and later[2] have been given the new name beidellite.[3] The agreement of the Arkansas bentonite with beidellite is shown by the analyses of Table IV.

This mineral beidellite agrees very well with the formula $Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$ the bivalent bases being in sufficiently small quantity to be disregarded in the formula. The water content is similar to that of montmorillonite and behaves in an identical manner.

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[1] E. S. Larsen, and E. T. Wherry, *Jour. Wash. Acad. Sci.*, **7**, 208–17 (1917).

[2] E. S. Larsen, and E. T. Wherry, *Jour. Wash. Acad. Sci.*, **15**, 465 (1925).

[3] Clarence S. Ross, and Earl V. Shannon, *Jour. Wash. Acad. Sci.*, **15**, 467 (1925).

TABLE IV

ANALYSES OF BEIDELLITE

	21	22	23	24	25	26
SiO_2	45.52	45.12	47.28	45.32	46.06	50.85
TiO_2	——	——	——	——	.84	——
Al_2O_3	27.52	28.24	20.27	27.84	12.22	28.81
Fe_2O_3	2.80	4.12	8.68	.80	18.54	——
FeO	——	——	——	——	.28	——
CaO	.52	.88	2.75	2.76	1.66	——
MgO	3.00	2.32	.70	.16	1.62	——
K_2O	——	——	trace	.12	——	——
Na_2O	——	——	.97	.10	——	——
H_2O	19.60	18.72	19.72	22.64	17.26	20.34
Total	98.96	99.40	100.37	99.64	98.48	100.00

21. Bentonite. Mine Creek, near Nashville, Howard County, Arkansas. Fine separation product. Purified by Clarence S. Ross. E. V. Shannon, analyst.
22. Bentonite, same, coarser product.
23. Beidellite, "leverrierite" gouge clay from Beidell, Sagauche County, Colo. E. S. Larsen and E. T. Wherry, *Jour. Wash. Acad. Sci.*, **7,** 208–17 (1917).
24. Beidellite, "leverrierite" gouge clay, Black Jack vein, Carson Dist., Owyhee County, Idaho. E. V. Shannon, *Proc. U. S. Nat. Museum*, **62,** Art. 15 (1923).
25. Iron-rich beidellite; Spokane, Washington.
26. Theoretical alumina end member to satisfy $Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$.

One other crystalline finely micaceous clay of high water content has been encountered in the course of the present study. This is a snow-white rather hard clay from Washoe, Nevada. It is slickensided and may be a gouge clay. It probably is not a bentonite. The analysis is given below together with Schaller's analysis of the pink clay from the lithium pegmatite of Pala, San Diego, California which is probably the same mineral.[1] The composition of these clays is that of halloysite but they exhibit the finely crystalline structure of the montmorillonite and beidellite before considered. The formula derived from the analyses can be stated as: $Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$. The clay from Nevada contains about $4\frac{1}{2}$ H_2O while that from California contains only $3H_2O$, the difference possibly being due to different conditions of the atmosphere at the time they were analyzed. One feature in which the white clay from Nevada differs from the montmorillonites and beidellites is that it retains 14% of water above 140°C. The constitutional water of kaolinite amounts to two molecules, the formula being written $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ or $H_4Al_2Si_2O_9$. Halloysite retains two molecules of constitutional water to a red heat so that its formula is commonly written as $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + nH_2O$. The latter formula equally well represents the clay from Washoe, Nevada.

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[1] Waldemar T. Schaller. U. S. Geol. Surv., *Bull.* **262,** p. 121.

TABLE V

ANALYSES OF CLAY FROM NEVADA AND CALIFORNIA, COMPARED WITH HALLOYSITE.

	27	28	29	30
SiO_2	37.40	43.62	40.09	40.90
Al_2O_3	34.04	35.55	35.58	34.66
Fe_2O_3	1.08	.21	trace	——
CaO	.60	1.02	.77	——
MgO	.64	.19	trace	——
MnO	——	.26	——	——
Li_2O	——	.23	——	——
Na_2O	——	.19	.10	——
K_2O	——	.03	trace	——
H_2O	26.40	18.88	23.61	24.44
Total	100.16	100.18	100.15	100.00

27. White slickensided clay from Washoe, Nevada. Earl V. Shannon, analyst.
28. Pink clay from gem-bearing pegmatite, San Diego Co., Calif. Waldemar T. Schaller, Analyst. *Loc. cit.*
29. Halloysite, Wagon Wheel Gap, Colo. Edgar T. Wherry, analyst. E. S. Larsen and E. T. Wherry. *Loc. cit.*
30. Calculated composition to agree with formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \cdot$ plus 2Aq.

Optical Properties

The following table gives the optical properties of the clay minerals that have been described in this paper.

TABLE VI

OPTICAL PROPERTIES OF THE CLAY MINERALS

	α	$\beta\ \gamma$	$\gamma-\alpha$	2ν	Optical Character
Montmorillonite from normal bentonites, analyzed[1]					
2 Ardmore, S. Dak.	1.495	1.520	.025		—
4 Otay, San Diego Co., Calif.	1.492	1.513	.021	16°-24°	—
5 Tierra Amarilla Grant, N. Mex.	1.51	1.53			—
8 Maricopa, Kern Co., Calif.	1.492	1.515	.023	15°-22°	—
9 Fort Steel, Wyo.	1.484	1.508	.024	13°-24°	—
10 Wisconsin, Texas	1.493	1.515	.022	7°-19°	—
11 Quilchena, B. C.	1.487	1.514	.027	18±	—
Montmorillonite from normal bentonites, analyzed.					
Rosedale, Alberta	1.492	1.514	.022	small	—
Rideout, Utah	1.478	1.500	.022	10°-16°	—
Montmorillonite from altered pegmatites[2]					

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[1] The numbers correspond with the analyses in Table I, pp. 88 and 89.

[2] The numbers correspond with the analyses in Table II, p. 90.

14 Montmorillon, France	1.503	1.527	.024		—
16 Embuda, N. Mex.	1.594	1.517	.023		—

Montmorillonite from fullers' earth[2]

17 Bainbridge, Ga.	1.512	1.535	.023	17°-25°	—

Montmorillonite from bentonite, with adsorbed potash[3]

[3] The numbers correspond with the analyses in Table III, p. 92.

19 Suifu, China	1.543	1.565	.022	12°-25°	—
20 High Bridge, Ky.	1.528	1.550	.022	15°-27	—

Beidellite from gouge clays and bentonite[4]

[4] The numbers correspond with the analyses in Table IV, p. 94.

21 Mine Creek, Nashville, Ark.	1.517	1.549	.032	16° ±	—
23 Beidell, Colo.	1.494	1.536	.042	small biaxial	—
24 Black Jack Vein, Owyhee Co., Idaho	1.488	1.527	.039	"	—
25 Spokane, Wash.	1.523	1.572	.051	"	—
Wagon Wheel Gap, Colo.	1.495	1.537	.042	"	—

Micaceous, crystalline "halloysite"[5]

[5] The numbers correspond with the analyses in Table V, p. 95.

27 Washoe, Nev.	1.540	1.550	.010	?	
28 San Diego Co., Calif.	1.495	1.518	.023	—	

The foregoing tables show that the montmorillonite from normal bentonites has indices of refraction that vary but little from the mean values that are $\alpha=1.493$, β and $\gamma=1.516$, and the montmorillonite from other sources shows nearly the same values. The potash-bearing bentonites are composed of montmorillonite with a higher indices of refraction since the water which tends to lower the indices has been displaced by potash. The beidellites are very likely to contain ferric iron which is present in varying proportions in all the samples analyzed. For this reason the indices of refraction are higher and more variable than in the montmorillonite, and the birefringence is also higher. The micaceous "halloysite" from San Diego, California, has optical properties that are very close to those of the other minerals described in this paper. The higher indices and lower birefringence of the clay from Washoe, Nevada, suggest that it may be a distinct mineral. The San Diego clay is believed to be distinct from halloysite though having the same chemical composition but it is possible that the Washoe clay is a true halloysite that happens to have visible crystallinity.

INFLUENCE OF COMPOSITION OF BODY AND GLAZE ON THE PHYSICAL PROPERTIES OF A TRUE PORCELAIN[1]

By Pyungtoo William Lee

Abstract

An effort to produce a higher quality of true porcelain at cones 10 to 12. Physical properties of body and glaze and their workabilities are observed. Tested for shrinkage, warpage, translucency, absorption and modulus of rupture.

Introduction

The purpose of this investigation is to obtain the possibility of producing a true porcelain of higher quality, chiefly, using domestic materials. The proper proportions and mixture of the different constituents and ingredients in the body and glaze have much to do with the quality of the ware. In solving the problem there are two things to be considered: the physical and chemical properties of their constituents, and their influences. This present investigation deals only with the physical properties and their influence.

The Layout of the Investigation

1. Raw Materials

The raw materials used in this investigation are as follows:

Canadian feldspar	Pa. Feldspar Co.
Flint	Ohio Silica Co.
English china clay	Moore and Munger's M.W.M.
Florida kaolin	Edgar Kaolin Co.
Whiting ($CaCO_3$)	Gilder's
Magnesium carbonate ($MgCO_3$)	
Boric acid (H_3BO_4)	

2. Preparation of Body

The three end members, (Nos. 1, 11, and 15) were thoroughly mixed by grinding in ball mills for 72 hours and screened through 150-mesh sieve. The other 12 members of the series were the combinations of the three end members. Two cups were cast from each member; then the slips were dried in the open air to the stage of plastic clay and used for jiggering cups and molding trial bars for modulus of rupture, absorption and translucency. The cups and trial pieces were dried to bone dryness in the gas heated drier and biscuited at cone 06. Necessary measurements for shrinkage, loss of weight and other observations were taken before they were glazed.

Glazing and Setting

The cups, both cast and jiggered, and two trial pieces for translucency and warpage were glazed with the following glaze at 20 ounces to a pint.

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[1] A thesis presented for the degree of Master of Science, Ohio State University (1922). Received November, 1925.

$$\left.\begin{array}{l}0.19\ \ K_2O\\ 0.7225\ CaO\\ 0.025\ \ MgO\\ 0.025\ \ BaO\\ 0.0375\ ZnO\end{array}\right\}0.7\ Al_2O_3\text{–}7.0\ SiO_2.$$

The cups and the trial pieces were dipped into the glaze with a slow motion. The thickness of the glaze was about $\frac{1}{32}$ inch. The glaze had a very little flowing action at the glost fire.

Placing in a Sagger and Kiln Setting The cups and bars (outside bottom of the cups and on side of the bars not glazed) were placed upon a sand bed in the sagger and the trial pieces for translucency and warpage were placed upon tiles in saggers.

Glost Firing The total firing period was 26 hours. More excess air was used during the period of water-smoking. The dampers were left wide open from the beginning of the firing until the kiln was completely cooled.

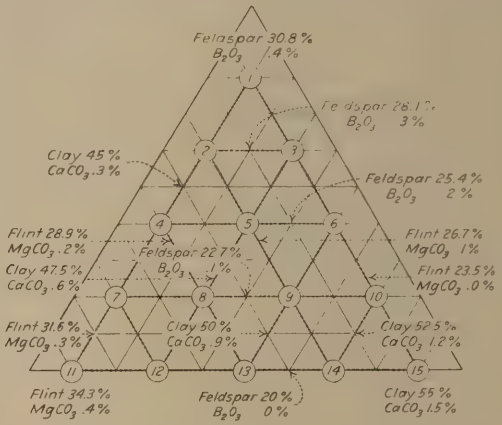

FIG. 1.—Shows the different bodies in a triaxial form and compositions of Series 4.

Tests

The tests applied in this series were for shrinkage, loss in weight, cross breaking and modulus of rupture, absorption, warpage and translucency.

The whiteness of the color was observed on glazed and unglazed bodies both cast and jiggered. The results are as follows:

Color The order of color in its clearness and whiteness is as follows: 8, 7, 11, 12, 13, 4, 9, 14, 15, 2, 3, 6, 5, 10, 1. A difference of color noticed even on the same composition which was due to the variation of the temperature and the kiln atmosphere. It may be possible to improve the colors of all bodies by firing with greater excess of air throughout the firing period.

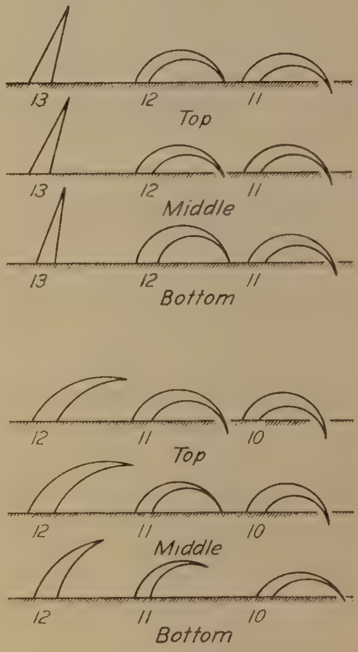

FIG. 2.—Observation of the cones. Cones outside of saggers shown above and those inside shown below.

Measurement of Shrinkage Only linear shrinkage was obtained from plastic to dry, dry to biscuit, and dry to glost. From these values the per cent of shrinkage, on dry bases, was calculated.

Measurement of Loss in Weight First the water content of each plastic body was determined, then the weights on dry bodies, biscuited bodies, and glost bodies measured from which the present loss in weights was calculated on a dry base.

Modulus of Rupture The unglazed and glost fired square bars were broken by Riehle Bros. T. M. Co. Cross Breaking Strength Machine. The length (L) between two supporting distances was 3 inches. This gave the value of cross breaking strength directly for a cross sectional area of the broken bars. From these values the modulus of rupture was calculated by using the formula

$M=\frac{3PL}{2bd^2}$.

P = weight required to break the bars
L = distance between supporters. (3 inches)
b = width of broken section,
d = depth of broken section.

These values were again interpolated for the value of one square inch.

Absorption Test The broken bars were weighed and boiled in water for over two hours, and then remained in water for more than 48 hours. These were again weighed and the per cent of absorption calculated by using the formula

$P=\frac{W-w}{w}\times 100$

where W = wet weight,
w = dry weight
P = per cent absorption.

Measurement of Warpage Two methods were employed for the measurement of warpage: One by observing the degree of warpage from cast and jiggered cups and another by measuring the height of the bending places of the trial pieces as shown in Fig. 3.

Measurement of Translucency

The translucency was measured by means of an electric light. At one end of a box was placed an electric light bulb. A tin plate was placed at one end of the box and in it was a hair crevice which transmitted the light. Tests were made by placing the trial pieces against the crevice and moving them from the thin to the thicker end. The line where the light ceased to be transmitted was noted and marked and then thickness of the body at this line was measured by a micrometer.

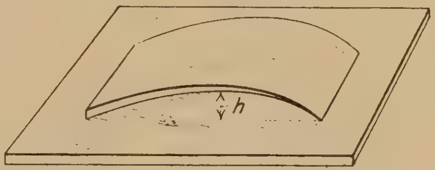

FIG. 3.

Comparisons

Numbers 8 and 7 are the best bodies and No. 8 has proved to be the best in working properties.

Comparing purity and whiteness of the colors with the American and French porcelains, Nos. 8 and 7 have proved superiority over American porcelain and No. 8 has approached very closely the best French porcelain.

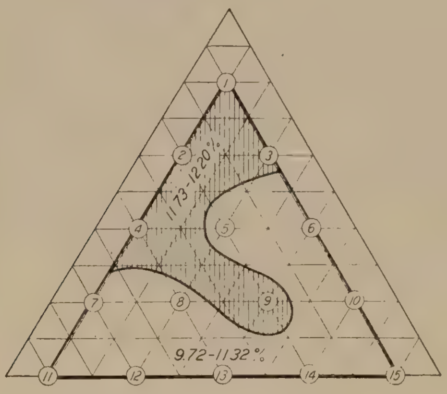

FIG. 4.—Per cent shrinkage on dry base.

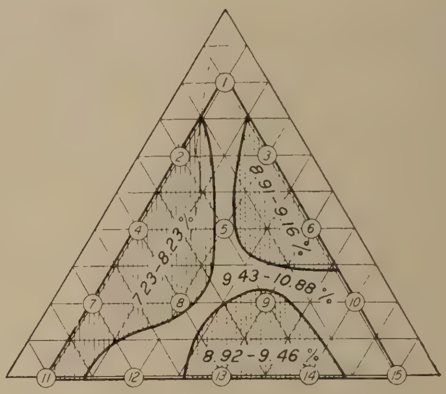

FIG. 5.—Per cent loss in weight on glost firing.

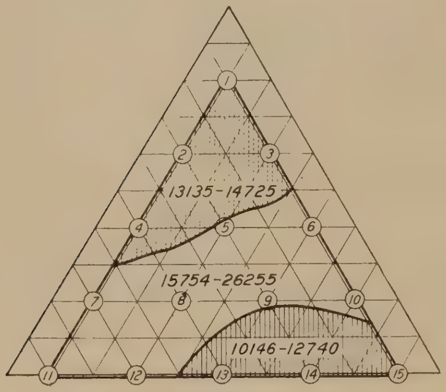

FIG. 6.—Modulus of rupture.

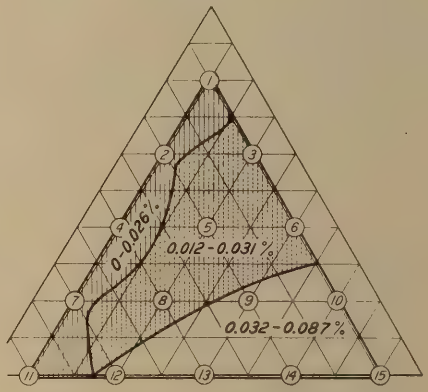

FIG. 7.—Per cent absorption

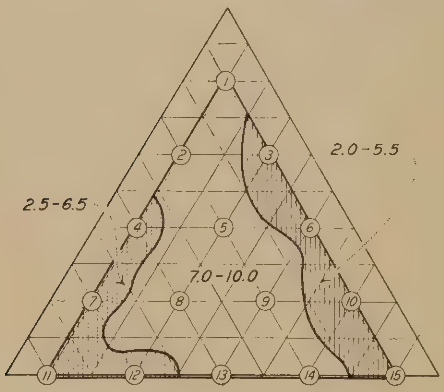

FIG. 8.—Warpage of Series 4.

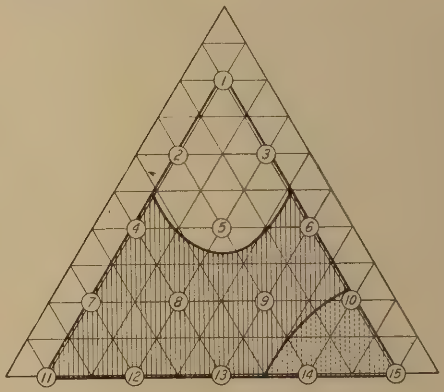

FIG. 9.—Translucency.[1]
Scale $\frac{1}{100}''$

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[1] Bodies 1, 2, 3, 5 are 12.00–12.40
Bodies 4, 7, 11, 8, 12, 6, 9, 13 are 11.18–11.23.
Bodies 10, 14, 15 are 11.20–11.90.

Conclusions

In this investigation the following general facts were observed:

1. The application of a glaze is better on jiggered than on cast bodies.

2. The warpage is always greater in the cast than in the jiggered bodies.

3. The translucency for the same composition is increased with the increase of temperature.

4. There is a temperature which produces the best color for a definite body. Below this point the color of the body will not fully develop and beyond it the color will be changed with other influences.

5. To obtain the best working conditions the total of alkaline earth fluxes must not be over 1%. If $MgCO_3$ is used to improve the color of the body it must not be more than 0.4%.

6. Vitrification is increased with the increase of feldspar and flint, and decrease of clay.

7. Translucency is increased with the increase of feldspar at the expense of flint and clay.

8. Loss in weight is increased with the increase of clay and decreased with the increase of flint.

9. Shrinkage is increased with the increase of feldspar and decreased with the increase of flint and clay.

10. The fusion point of any glaze can be lowered by long and fine grinding, but it will tend to increase the tendency to crazing if the coefficient of expansion of the body and glaze are not the same.

11. The zinc content in the glaze increases the white color but decreases the translucency and produces a rough surface.

In conclusion it is safe to say that No. 8 in the Series 4 which proved superior to the American porcelain and ranked close to the French met all conditions above normal that a true porcelain might require.

Bibilography

On Bodies

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"The Value of Physical Property of a Clay," **1**, pp. 36-37.

"Mechanical Analysis of a Clay," **1**, pp. 41-44.

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From Other Literature

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On Glazes

From *Collected Writings* of Herman A. Seger

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INFLUENCE OF Fe_2O_3 AND TiO_2 ON PURE CLAYS[1]

By Adolph Harmon Kuechler

Abstract

In this thesis, the effect of small additions of TiO_2 and Fe_2O_3 on the fusion temperature of kaolin and fire clay is investigated.

Introduction

In this thesis, the effect of small additions of TiO_2 and Fe_2O_3 on the fusion temperature of kaolin and fire clay are investigated. The object is to determine the action of Fe_2O_3 and TiO_2, in clays and to secure evidence on whether chemical composition or mineral classification shall be made the basis for the estimation of the refractoriness of clays.

Effect of Titanium

Several ceramic phenomena have been accredited to the function of titanium in clays. It has been shown that it exerts a fluxing influence, but to what extent and in what manner has never been definitely determined.

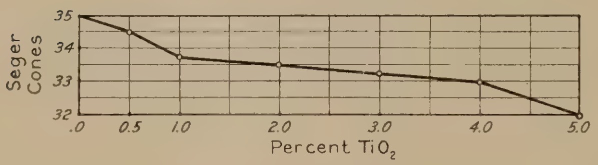

Fig. 1.—Kaolin and titanium oxide by H. Ries.

H. Ries[2] has shown that even small amounts of titanium lower the refractoriness of a clay. In his experiments a white firing sedimentary clay fusing at cone 35 was mixed with amounts of ½, 1, 2, 3, 4, and 5% of very finely ground rutile. These mixtures were then formed into small cones and tested in the Deville furnace. The results of these tests are shown in Fig. 1.

Rieke[3] made up a series of mixtures of chemically pure TiO_2 and Zettlitz kaolin, determining their fusion points with the following results:

Kaolin Per cent	TiO_2 Per cent	Cone of fusion	Kaolin Per cen	TiO_2 Per cent	Cone of fusion
100	0	35	40	60	20
90	10	30	30	70	+20
80	20	−26	20	80	−26
70	30	20	10	90	26
60	40	−20	0	100	−27
50	50	19–20			

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[1] A thesis presented for the degree of Bachelor of Ceramic Engineering, Ohio State University, (1924).

[2] *N. J. Geol. Surv.*, **6**, 71 (1904).

[3] *Sprechsaal*, **41**, 406 (1908).

C. K. Bryce studied the effect of TiO_2 on the pyrometric value of a clay as a thesis at Ohio State University in 1909. He found in using Georgia kaolin, Laclede-Christy fire clay and Standard ruby rutile that within the limits of the investigation titanium acts as a neutral flux. Within the limits of the experiment, no eutectic points were observed in the melting point curve and no apparent chemical changes. See Fig. 2.

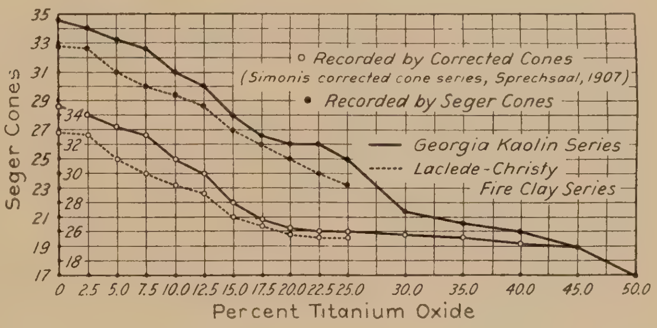

FIG. 2.—Melting points of TiO_2 and clay mixtures.

Effect of Iron Oxide

Dr. Ries found that iron oxide is a fluxing impurity, lowering the fusion of a clay, and this effect will be more pronounced if the iron is in a ferrous condition or if silica is present. A low iron content is, therefore, desirable in refractory clays, and the average of a number of analyses of these shows it to be 1.3%. Brick clays, which are usually easily fusible, contain from 3 to 7% of iron oxide.

A. V. Bleininger and G. H. Brown[1] state that iron oxide in the finely divided condition is one of the most potent fluxes. When present in the form of coarser particles, occurring as siderite or pyrite, its effect is not so marked, since evidently the action is proportional to the surface factor, *i.e.*, the fineness.

At the high temperatures to which refractories are exposed the ferric oxide of the clay dissociates to one of its lower forms. According to Le Chatelier[2] this dissociation takes place at 1300°, according to White and Taylor at 1200°, and to P. T. Walden[3] at 1350°C. The last named value represents probably the most reliable results. At this temperature the dissociation pressure reaches 160 mm., which is equal to the oxygen pressure of the air. Ferric oxide hence cannot exist above this temperature. It does not seem probable that the magnetic oxide $3Fe_2O_3 = 2Fe_3O_4 + O$ would persist at these high temperatures in contact with a silicate of the first clay type. The reduction under these conditions very likely results in FeO, which at the temperatures involved would at once combine with silica to form ferrous silicate. This change is hastened by the reducing conditions which usually prevail in the atmosphere of firebrick kilns. Larger lumps of iron oxide embedded in the clay mass may consist in part of ferro-ferric and ferrous oxide, but the finely divided oxide may be assumed to be only FeO. Reaction between FeO and SiO_2 progresses rapidly, and owing to the low fusion temperature of the ferrous silicate the resulting slag is very corrosive and attacks the clay vigorously.

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[1] U. S. Bur. Stand. *Tech. Paper*, **7**.

[2] "High Temperature Measurements," p. 246

[3] *Jour. Amer. Chem. Soc.* **30,** 1350

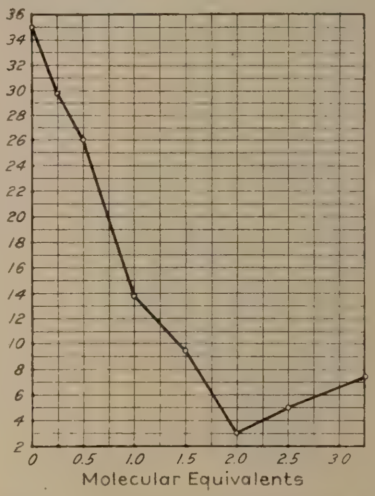

FIG. 3.—Effect of additions of FeO to Al_2O_3–$2SiO_2$.

From the work of Cramer[1] it appears that iron oxide is an active flux with clays of the formula Al_2O_3–2.5 SiO_2, while it is less active in fire clays approaching more closely the kaolin formula. The addition of 0.2 equivalents of Fe_2O_3 sufficed to lower the softening temperature of a clay mixture of the formula Al_2O_3–$2.5SiO_2$ from cones 34 to 27.

The viscosity of ferrous silicates is quite low, as has been shown by Greiner, while ferric oxide acts in the opposite direction and increases the viscosity of silicate fusions. The softening temperatures given by Hoffman[2] for various ferrous silicates are as follows:

4 FeO–SiO_2	1280°C
3 FeO–SiO_2	1220
2 FeO–SiO_2	1270
3 FeO–2 SiO_2	1140
4 FeO–SiO_2	1120

Figure 3 gives the results obtained by Rieke[3] on the fluxing action of FeO in a mixture of Al_2O_3–2 SiO_2.

Materials Used The materials used are: Florida kaolin, having the following composition:

Loss on ignition	14.86
SiO_2	45.67
Al_2O_3	38.45
Fe_2O_3	.75
TiO_2	.10
MgO	.05
K_2O	.06
	99.94

Fe_2O_3, containing 97.8% iron ore and 2.2% impurities.
TiO_2, (finely ground rutile) manufactured by the American Rutile Co.
Fire clay with the following analysis:[4]

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[1] "Wirkung der Flussmittel in Tonen." *Tonind, Ztg.*, No. 40-41 (1895).
[2] *Trans. Amer. Inst. Min. Eng.*, p. 682 (1899).
[3] *Sprechsaal*, p. 231 (1910).
[4] From Kier Fire Brick Co.

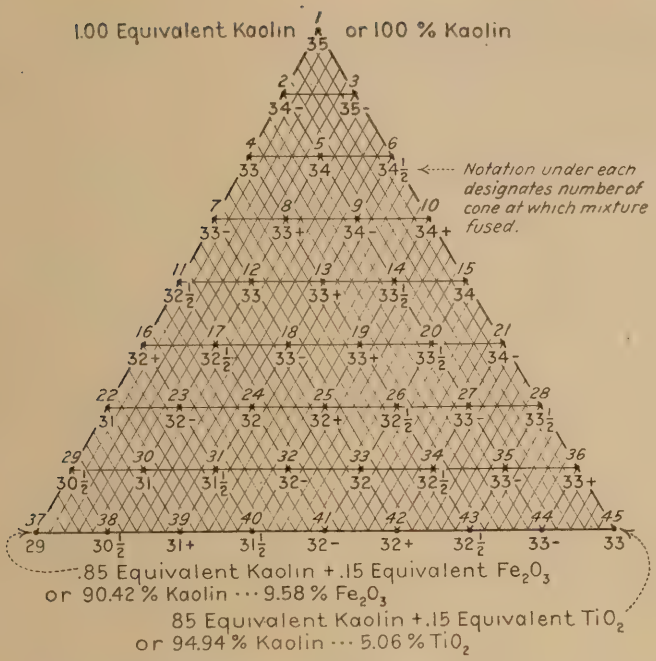


FIG. 4.—Presenting data on fusion temperatures of kaolin Fe_2O_3–TiO_2 mixtures.

Ign. Loss	13.52%
SiO_2	43.10
Al_2O_3	38.94
Fe_2O_3	1.74
TiO_2	2.80
CaO	0.16
MgO	0.08
Alkalis	0.19
	100.53

Materials for cone plaques:

	Per cent
Calcined bauxite	50
Calcined Georgia kaolin	25
Florida kaolin	25

The molecular formula of the Florida kaolin is:

$$\left.\begin{array}{lr} 0.0016 & K_2O \\ 0.0032 & MgO \\ 0.0032 & TiO_2 \end{array}\right\} \begin{array}{l} 1.00\ Al_2O_3 \\ 0.0125\ Fe_2O_3 \end{array} \left\{\begin{array}{l} 2.013\ SiO_2 \\ 2.196\ H_2O \\ \text{Eq. Wt. } 265.6 \end{array}\right.$$

The molecular formula and equivalent weight of the fire clay is:

$$\left.\begin{array}{l} 0.008\ CaO \\ 0.005\ MgO \\ 0.092\ TiO_2 \\ 0.005\ \text{Alkalis} \end{array}\right\} \begin{array}{l} 1.000\ Al_2O_3 \\ 0.029\ Fe_2O_3 \end{array} \left\{\begin{array}{l} 1.796\ SiO_2 \\ 1.972\ H_2O \end{array}\right. \quad \text{Eq. Weight} = 259.1$$

The composition for each point on the triaxial, Fig. 4 is next determined.

Point 1 consists of 1.0 equivalents of Florida kaolin.

Point 37 consists of:

$$\begin{array}{lr} .85 \text{ equivalents of Florida kaolin or} & 265.64 = 225.50 \\ .15 \text{ equivalents of } Fe_2O_3 \text{ or} & 159.60 = \underline{\ 23.93} \\ & 249.43 \end{array}$$

and since 100 grams are to be made up for each point,

$$\frac{225.50}{249.43} \times 100 = 90.42 \text{ grams kaolin.}$$

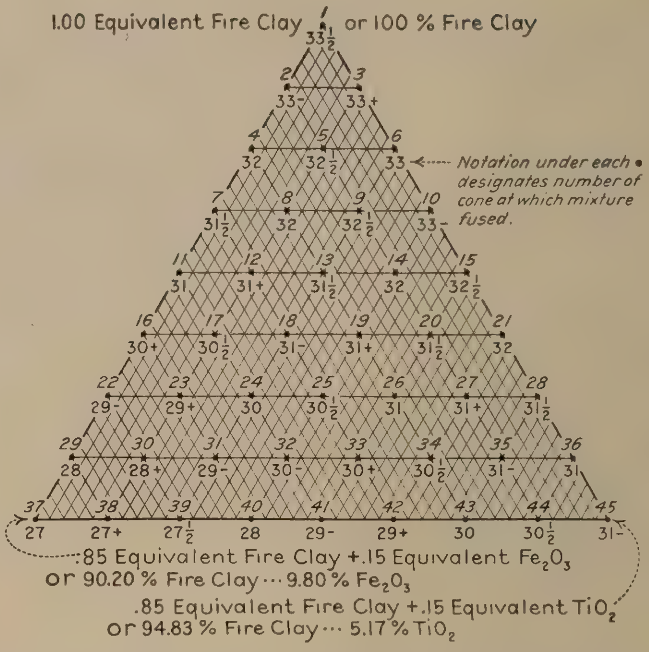
$$(37) \text{ will have } \frac{23.39}{249.43} \times 100 = \ 9.58 \text{ grams } Fe_2O_3.$$

The mixtures for all the different points on the triaxial were determined in this manner.

The materials, after being weighed out, were thoroughly dry ground and mixed with a mortar and pestle.

The materials were ground to pass a 80-mesh screen.

After adding sufficient water to give the mixture the best working qualities, cones 1⅛ inches in length were formed.



Notation under each • designates number of cone at which mixture fused.

FIG. 5.—Presenting data on fusion temperatures of fire clay Fe_2O_3–TiO_2 mixtures.

The cones were held in the plaques with calcined Al_2O_3, each plaque holding seven cones.

About one and one-half hours were required for a firing.

Results

The binary graph containing Fe_2O_3 additions (Fig. 6) tends toward a straight line. Iron is very susceptible to firing conditions, *i.e.*, ferrous iron is more of a flux than ferric iron, and this seems to account for the irregularities. Approximately 10% of Fe_2O_3 lowers the fusion temperature of kaolin and fire clay 6 and 6½ cones respectively.

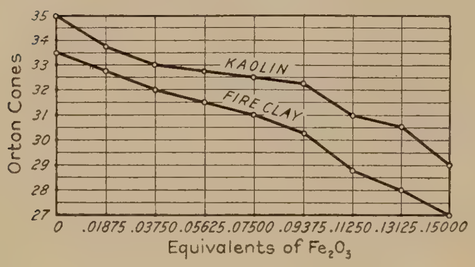


FIG. 6.

The binary graph containing TiO_2 additions (Fig. 7) is a straight line in the case of kaolin but is a little irregular in the case of the fire clay. The fluxing action of the iron content of the fire clay seems to account for this irregularity. About 5% TiO_2 lowers the fusion temperature of the kaolin and fire clay 2 and 3 cones respectively.

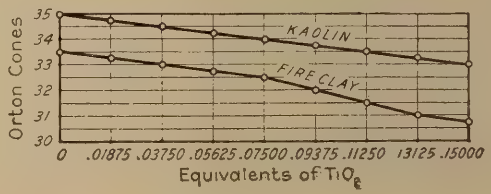


FIG. 7.

The binary graph containing Fe_2O_3 additions (Fig. 8) is merely interesting in that no eutectic forms. Again, in this case, the graphs tend toward a straight line.

Conclusions

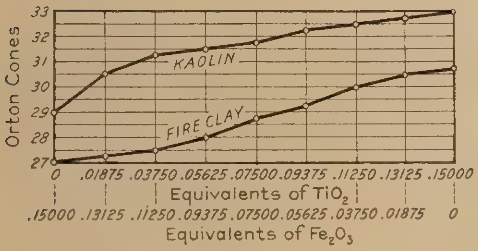


FIG. 8.

The results seem to indicate that there is about 6 to 6½ cones lowering of deformation period with the addition of about 10% Fe_2O_3, also that there is a deformation of 2 to 3 cones for an addition of about 5% TiO_2. The fluxing action of the Fe_2O_3 and TiO_2 appear to be about the same on a percentage basis.

This study failed to reveal an eutectic. (See Figs. 4 and 5.)

ELIMINATION OF LIMESTONE FROM CLAY[1]

By Roy A. Horning

Abstract

A successfully tried method of stone elimination is described.

Introduction

In this problem, it is well to take into consideration (1) What percentage of limestone is present, (2) The physical nature of stone and clay and (3) What effect will finely ground limestone have on the clay in question when distributed through the mass. Where the percentage of limestone is high the problem becomes very difficult, but if the percentage is not too great it may be attacked in several ways.

Many schemes have been devised for the removal of limestone and some have been fairly successful. Where the clay is friable and fairly dry, rubber covered rolls and screens are very good. This process will eliminate about 95% of the stone if it is not too hard. However, with this method it is not practical to screen some clays finer than $\frac{1}{4}$ inch and this often is not fine enough. This method has some merit, but its chief defect is that it will not work the year around, especially when the clay is wet.

The physical nature of both the stone and clay really determines the type of process that can be used. Obviously a shale would have to be treated differently from a clay.

Method Used at Lancaster

We assume that any stone is objectionable and should be eliminated if possible. Our trials of many schemes have shown that a certain per cent can be eliminated but that it is doubtful if 100% elimination is possible.

When all the elimination that is practical has been accomplished, fine grinding is used, reducing the percentage that is left to a very fine powder, thus rendering it less harmful.

The details of the process is given as follows:

1. Care is exercised in the clay pit as far as is possible to avoid the stone.

2. When the cars are dumped into the feeder the clay is retained on a steel grid temporarily, the clay being worked through the grid and the larger stones thrown out by hand. The smaller stones go through to the grinder.

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[1] Recd. Dec. 31, 1925.

See Bibliography of literature on pebbles removal by Fred T. Heath, *Bull. Amer. Ceram. Soc.*, **4** [4] 165-88 (1925).

3. The clay and smaller stones are fed into a pair of conical rolls. One roll is threaded and one roll is plain. The rolls are spaced about $\frac{1}{4}$ inch apart. Practically all stones larger than one inch which constitute about 85% of the stones in the clay are thrown out by the threaded roll. The smaller stones are crushed to size from dust to that of a large pea. The clays are passed from the conical rolls to a large storage and mixing pile. Here all the different strata of clay are thoroughly mixed. The mixing of these various clays in this manner gives a uniform product and also distributes the stone throughout the material. From the storage pile the clay is reclaimed by an underground conveyor and passed onto a clay cleaner.

The clay cleaner consists of two parts, a large pug mill and a set of smooth rolls. The clay enters the cleaner at one end where it is mixed with the proper amount of water. As the clay is worked on down to the other end it is thoroughly pugged. A large wiper at the discharge end of the machine pushes the pugged clay through a small opening into the crux of the rolls. These rolls are superimposed and both run at a speed of about 260 r.p.m. The rolls, being only 18 inches in diameter have a large angle of nip, hence the wet and smooth stones with a coating of clay on them are not readily gripped by these surfaces. Consequently, the stones which are about $\frac{1}{2}$ inch in size ride on the crux, being passed out to the end by an oscillating finger and discharged. Stones too small to be retained are readily crushed to a very fine mesh. These rolls are kept a little less than $\frac{1}{16}$ inch apart. To use these rolls successfully, they must be kept very smooth and uniform. To do this they are reground after every million brick.

Clay passing through the clay cleaner is then ready to go on to the brick machine pug-mill where all these bits of stone dust are intimately mixed throughout the clay.

The result of this combination of processes has been a salvation for the brick plant on which it is being used. Today, out of a clay that at one time was utterly useless on account of the vast quantity of stone in it, we can produce a very high grade sandmolded brick. This system has been in operation in its entirety for six months and so far we have had no indication of limestone in our product.

Removal of Pyrites

Before going any further it should be mentioned that while we have concerned ourselves mostly with limestone there is also present in this clay a very large quantity of iron pyrites. The pyrites are in cubical form and range from $\frac{1}{16}$ to $\frac{1}{2}$ inch. Conical rolls will not do very much for them. If these pyrites pass on to the brick without being ground very fine they will cause the brick to crack badly and render them valueless.

Cost of Operation

The labor required practically is the same no matter which system is used. One extra man is required to feed the belt in the storage system, assuming that the production does not exceed 8500 brick per hour. The usual hoist operator tends the feeder and the conical rolls and the regular man at the pug-mill runs the clay cleaner.

The power required to operate the feeder and conical rolls is about 60 to 75 horsepower, which is the same for a similar feeder and an ordinary disintegrator. The clay cleaner uses 75 to 100 horsepower, depending on conditions which vary a great deal. This is about 50% more power than would be required to operate an ordinary closed end pug-mill and its feeding conveyor.

The investment charge on this equipment is somewhat higher than the ordinary equipment, but on an output of a million a month it is very small.

Benefits Derived

On the other side of the ledger against the added expense of power and overhead are (1) improved quality of ware and (2) reduced losses. The improved quality is especially important where you have competition. Better brick means more business and a stability of trade. How much this means in dollars and cents is for each individual to determine for himself.

The item of losses in manufacture is one that stays at home for constant observation and in this item is the dollar and cents benefit. It was nothing unusual for this plant to throw away from 50,000 to 75,000 bricks out of one kiln of 245,000 on account of the limestone and iron pyrites. This would not happen with every kiln, but at times when we would run unwittingly into a deposit of half-disintegrated limestone. The pyrites no one ever sees until the brick are fired. In every kiln we would haul to the dump from 5,000 to 10,000 brick broken by these stones, to say nothing of the rebates that had to be made to customers to whom we had unknowingly delivered some of these defective brick.

In two cases we had to tear down the walls of a partially built structure and rebuild them, paying for the brick and labor in doing so. Such expenses as these are absolutely eliminated since we have installed this process. Incidentally, we are selling more brick at a better price with a direct saving of about 50 cents per thousand in the cost of manufacture.

Recapitulation of Process

1. Careful digging of clay.
2. Careful feeding of the conical rolls.
3. Elimination of all stones larger than one inch as far as possible.
4. Grinding all stones through the conical rolls as small as possible.
5. Thorough mixing to prevent slugs of finely ground stone passing into the brick machine, subsequently getting a large amount in a single brick.
6. Regrinding through $\frac{1}{16}$ inch opening all material going into the brick.
7. Repugging finely ground clay and stone dust to get a uniform distribution.

Lancaster Brick Company,
Lancaster, Pa

INSULATION OF CERAMIC KILNS[1]

By Walter Kennedy

Abstract

Description and results of insulation are given.

One of the many important problems with which the ceramic engineer of today has to contend is the steadily increasing cost of fuel and consequent higher production costs. Ceramic engineers have for a long time generally agreed that at least 25% of the heat developed in firing a kiln is lost by conduction through the brickwork and by radiation from exposed surfaces. A considerable amount is also absorbed in the large volume of brickwork used in the walls, bottoms and flues and in the earth upon which the kilns are built. Raymond M. Howe, in a paper read before the Kentucky and Southern Ohio Branch of the Refractory Manufacturers' Operatives' Institute in January, 1923, advanced the following heat distribution ranges for the ordinary downdraft kiln:

	Per cent
Lost in unburned ash	1.6– 3.9
Taken up by kiln and lost by radiation	33.3–59.7
Stack loss	27.3–57.1
Used in firing ware	8.0–19.5

As an indication of the vast amount of heat absorbed in the earth underneath kilns, one Missouri firebrick manufacturer who tore down a kiln and had occasion to excavate twelve feet below the ground level, found the earth there too hot to touch two weeks after the last kiln of ware had been drawn. Numerous similar instances have come to our attention.

Probably the first attempt at reducing radiation losses from kilns was the building of very thick walls. Walls from 4 to 6 feet thick have been constructed and while they do reduce the radiation loss during the firing, the great mass of brickwork which must be heated assimilates nearly as much heat as would be lost by conduction through a thinner wall. Furthermore, the thick walls are expensive in material and labor and occupy needed space. Even had this method been found satisfactory, it would obviously not be feasible on crowns, due to the excessive weight.

Another method tried was the so-called "dead-air space" built into kiln walls. This method has been used satisfactorily for refrigeration work but at the temperatures employed in firing brick this artifice defeats its own purpose because the hot surface of the air space radiates heat so rapidly that a greater amount is lost across the space by radia-

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[1] Presented before meeting of Pittsburgh Section Oct. 20, 1924. Recd. Oct. 25, 1924.

tion than would be conducted were the space to be filled with material of relatively high conductivity, such as fire brick. The quantity of heat passing through a portion of a solid wall by conduction depends on the difference between the temperatures of the two planes limiting the portion of the wall, while the quantity of heat that passes by radiation across the air space in the wall depends on the fourth power of the absolute temperatures of the surfaces enclosing the air space. Therefore, in the case of the heat passed by conduction through a solid wall, the loss remains approximately the same as long as the relative temperatures of the two limiting planes remain constant, no matter what may be the actual temperatures of the two planes. On the other hand, the heat passing across the air space by radiation and convection increases rapidly with the temperatures of the enclosing surfaces, although the difference between these temperatures may remain constant.

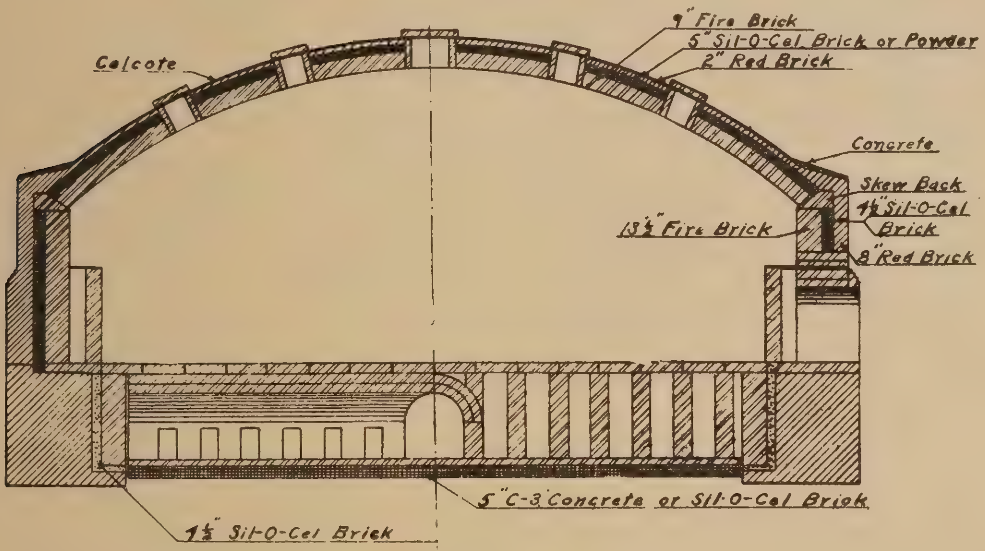

FIG. 1.—Method of insulating R.D.D. Kiln.

This subject is gone into in considerable detail in the U. S. Bureau of Mines, *Bulletin*.[1] This principle explains why hollow tile, while very satisfactory in ordinary building construction, affords no insulating value if used in high temperature equipment. Another illustration of this principle is the thermos bottle, in which liquids can be kept cold for 72 hours and hot for only 24 hours.

Characteristics of Insulation

It is now generally accepted that the only satisfactory method of reducing heat losses through the walls of any high temperature equipment is to install as a component of the wall a layer of material having a low conductivity and a low specific heat. Briefly, the ideal insulation for kilns or other equipment where analogous conditions prevail, should have the following properties:

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[1] Kreisinger and Ray, "Flow of Heat through Furnace Walls," U. S. Bur. Mines, *Bull.*, 8 (1912).

1. High heat insulating value.
2. Sufficient refractoriness so as not to change form or lose its efficiency when subjected to high temperatures.
3. Sufficient mechanical strength to resist wall strains due to expansion and contraction of the brickwork with changing temperatures.
4. Approximately the same coefficient of expansion as the brickwork.
5. Light weight (desirable for crown insulation).

Thorough Insulation Standard in Tunnel Kiln Construction

Continuous tunnel kilns, because of the great area of the exposed surfaces, would be very wasteful of heat due to conduction and radiation unless insulation were used. In fact, the absolute necessity of insulation for this equipment is so obvious that the writer does not know of any attempt ever having been made to operate tunnel kilns without insulation. From 9 to 12 inches of insulating powder is used over the crown and from 4 to 6 inches of insulating brick or powder in the side walls.

The tunnel kiln of the Bradford (Pa.) Brick and Tile Company has been described.[1] At a point in the kiln where the internal temperature just beneath the crown is 1980°F, the temperature through the 9-inch firebrick arch is 1450°F. The temperature on the outside of the 9 inches of insulating powder is 150°F. This is an excellent practical demonstration of the effect of insulation.

Methods of Insulating Periodic Kilns

This paper will be confined particularly to periodic kilns. The larger portion of the heat loss through insulated kilns is naturally sustained through the crowns due to the relatively thin construction which must be used to obviate having too much weight on the crown itself. Insulating brick weigh only 1¾ pounds each and this is so slight as to be practically negligible as far as its effect on the crown is concerned.

Side walls of periodic kilns are usually insulated with 4½ inches of insulating brick. Insulating powder is sometimes used for this purpose also. In a wall 27 inches thick, 13½ inches of refractory is used in front of the insulation and 9 inches of brick on the outside of the insulation. The walls can be bonded through the insulation by the use of either 9-or 13½-inch firebrick headers. Another method which has been perfectly satisfactory is the use of metal wall ties, consisting of crimped metal strips 12 inches long extending through the insulation course and approximately 4 inches into the other brick on either side.

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[1] *Brick and Clay Rec.*, Dec. 27, 1921.

The usual method of insulating bases is to use either one or two 2½-inch layers of insulating brick or five inches of insulating concrete (the latter being composed of calcined insulating material and Portland cement).

Advantages of Kiln Insulation

The most tangible advantage of insulation in kilns, and the one most readily convertible into dollars and cents savings, is the reduction in fuel bills. Other advantages which result are, however, considered by many users of insulation to be of more importance in the aggregate than the direct saving in fuel.

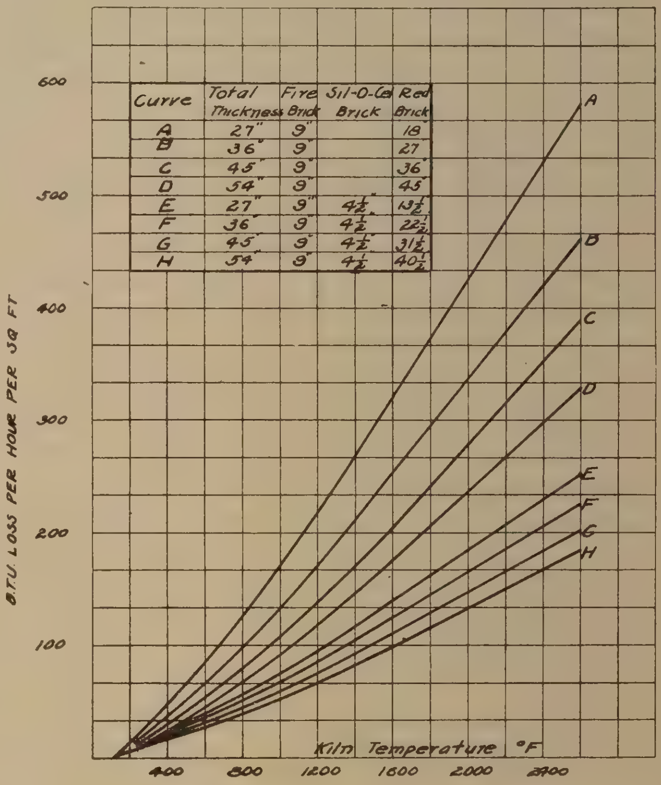
(a) Improved Quality of Firing It is a logical result of insulation, due to the blanketing effect of the insulating material, that the heat which cannot escape through bottoms, walls, and crowns, will naturally tend to distribute itself more uniformly through all parts of the kiln. In uninsulated kilns it is often necessary to force the fires and overfire near the fire-pockets and at the tops in order to bring more remote sections of the kiln (at the center of the load and at the bottom) up to the required finishing temperature. One refractory plant in the Pittsburgh district reduced the percentage of soft brick from 1.2% to 0.25% after insulating crowns and bottoms with Sil-O-Cel brick. Cones 6 and 7 were put down in the bottom of this kiln instead of cone 4 before insulating and this was accomplished without increasing the temperature at the fire-pockets. Insulated kilns are not susceptible to atmospheric conditions, which is especially important in climates where wide variations in temperature are encountered.

(b) Reduction in Firing Time Considerable reductions in firing time are effected by thorough insulation of kilns, which reduces the labor cost of firing and increases the kiln turn-over. At one plant where the bottoms and crowns were insulated the firing time was reduced from an average of 163 hours before insulating, to an average of 135 hours after insulating. This reduction of over one day amounts to a considerable item in a year's time. For instance, using the above figures as a typical example, the reduced time necessary for firing would enable ten insulated kilns to be fired off and to produce the same amount of ware as previously turned out of twelve uninsulated kilns. The result is that with the same kiln equipment, insulation will increase production considerably without additional expense for building kilns. This additional kiln capacity is always expensive to obtain by any other method.

(c) Longer Life of Crowns, Walls and Fire Pockets

In one or two isolated cases insulated crowns have given trouble but in these instances it was found to be due to faulty construction rather than to any fundamental factors governing the feasibility of insulating. The crown being exposed to maximum temperatures should naturally always be carefully built of a good quality refractory, the failing point of which under a load is reached at a considerably higher temperature than is required or will be reached in firing the kiln of ware. Where a good refractory is used there is no danger in insulating. Crowns which have been insulated for from six to eight years are still in excellent condition. In fact, it is now quite generally conceded that the effect of insulation is to increase the life of the crown brick due to the fact that the insulation results in a more uniform temperature throughout the 9-inch crown, with a natural reduction in internal stresses and strains and resultant cracking. Similarly, in the side walls of kilns, insulation prevents excessive temperatures from penetrating to the outer wall of common brick.

The necessity of forcing fires is obviated to a great extent by the use of insulation and the life of the fire-pockets is considerably lengthened.



Curve	Total Thickness	Fire Brick	Sil-O-Cel Brick	Red Brick
A	27"	9"		18
B	36"	9"		27
C	45"	9"		36"
D	54"	9"		45"
E	27"	9"	4½"	13½
F	36"	9"	4½	22½
G	45"	9"	4½"	31½
H	54"	9"	4½	40½

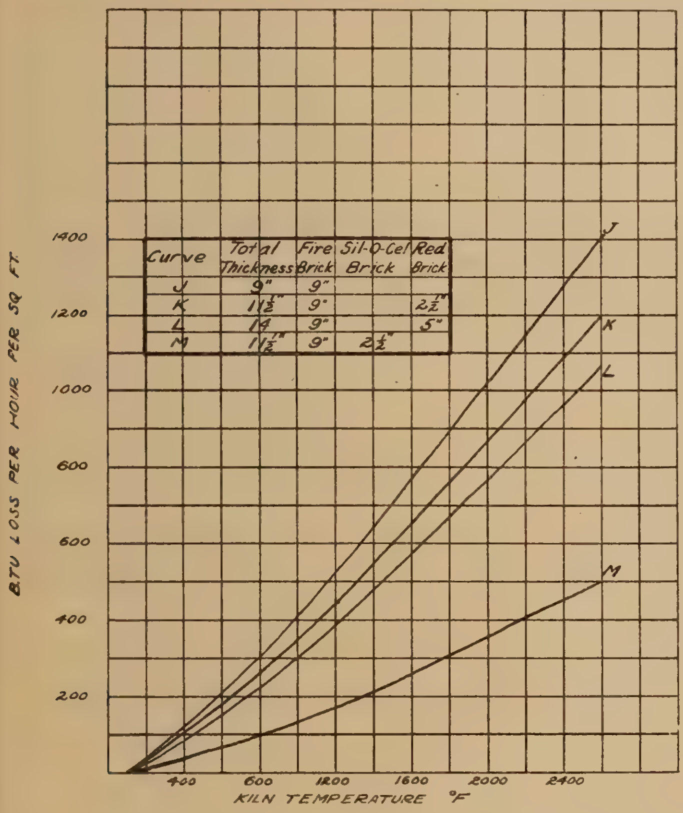
Fig. 2.—Comparative heat losses through insulated and uninsulated kiln walls.

Savings in Fuel

In practically every case where insulation has been used in kilns, careful records have been kept of fuel consumption and comparison made with records on the same kilns before insulating or with records on uninsulated kilns of the same size. While in some cases the savings have been found to be as high as 20% for thoroughly insulated kilns, it is generally conceded that from 16 to 17% is a very conservative figure. Most of the saving is undoubtedly effected by the crown insulation. Due to the fact that thinner side walls can be built, the cost of including insulation in side walls is little if any more than if insulation were not used. Base insulation, in addition to effecting considerable fuel saving, is an important factor in increasing bottom temperature and improving the quality of firing. Figure 2 shows the comparative B.t.u. loss through insulated and uninsulated kiln walls of various thicknesses. Similarly, Fig. 3 shows the comparative losses through various crown constructions.

Kilns for firing practically all kinds of ceramic products have been successfully insulated, including fire brick, common brick, paving brick, sewer pipe, pottery, and various kinds of tile, terra cotta and porcelain.

In some cases, of course, it is difficult to measure definitely the fuel savings which are being secured by insulation, due to a haphazard system of coal distribution or for some other reason. The fact that the insulation is saving fuel is very apparent, however, in every case. A comparison of exterior temperatures of insulated and uninsulated crowns will give a good indication of what is being accomplished. In Fig. 4 is shown the comparison in temperatures of insulated and uninsulated crowns, these curves being plotted from actual readings taken by the ceramic engineer of a representative plant.[1] Exterior crown temperatures of kilns built in the open are affected greatly by atmospheric conditions. Wind velocity is a particularly important factor. On a comparatively calm day the temperature of a crown may be 250°, while on a windy day, other conditions being the same, the temperature may be only 200°. More heat will be lost on the windy day, however,



Curve	Total Thickness	Fire Brick	Sil-O-Cel Brick	Red Brick
J	9"	9"		
K	$11\frac{1}{2}$"	9"		$2\frac{1}{2}$"
L	14	9"		5"
M	$11\frac{1}{2}$"	9"	$2\frac{1}{2}$"	

FIG. 3.—Comparative heat losses through insulated and uninsulated kiln crowns.

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[1] J. H. Kruson, A. P. Green Fire Brick Co., Mexico, Mo.

than on the calm day, as in the former case the heat is carried away more rapidly.

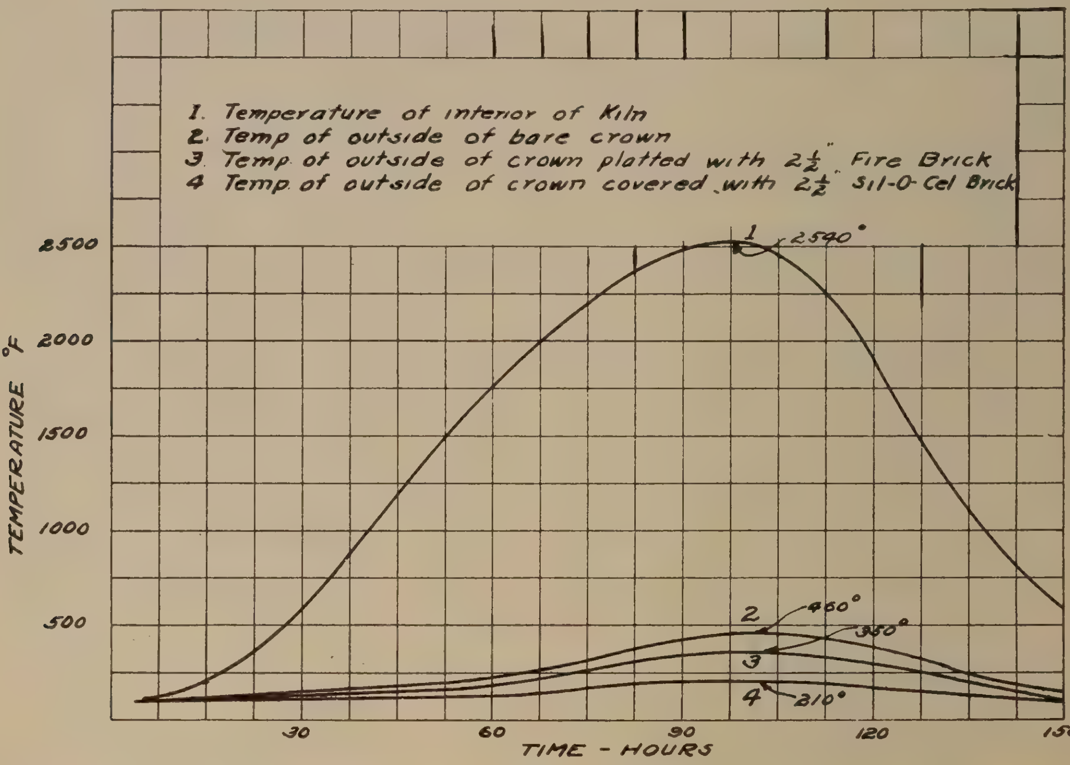

FIG. 4.—Comparison in exterior, temperatures on insulated and uninsulated kiln crowns.

Furthermore, in a number of cases where old kilns were insulated, it was found necessary to reduce the grate area to eliminate the danger of over-firing. The improved quality of ware and the reduction in the firing time are always conclusive evidence of the economy of insulating.

CELITE PRODUCTS COMPANY,
CHICAGO, ILLINOIS.

ERRATA: H. H. Clark, *Jour. Amer. Ceram. Soc.*, **8** [10] 623-25 (1925). Page 624, line 36, decimal points were omitted and sentence should read: "The pieces were of sizes varying from 3½ square feet to .3 square foot; 8 pieces to 100 pieces per load".

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ORIGINAL PAPERS

AN ACCELERATED ABRASION TEST[1]

BY CARL H. GEISTER[2]

ABSTRACT

A suitable abrasion apparatus is described which is capable of measuring the wear resistance of flooring materials having widely varying physical properties. The requisite conditions of wear necessary to produce results comparable to those obtained in actual service are given. Other abrasion methods and their shortcomings for use in this problem are summarized.

Introduction

An abrasion machine was devised to produce accelerated wear during an investigation on floor tile, which is being carried on at Mellon Institute. This machine was designed particularly for testing flooring materials, because no satisfactory method had been previously developed which was adaptable to producing wear in all types of floor coverings in accordance with the required conditions.

Requisite Factors of Wear

Abrasion of floors in service is mainly attributed to foot traffic. The average pedestrian, in the course of taking a step, strikes the floor with his heel, causing a definite impact shock. Slipping results when he shifts his weight to the sole and twists the foot in continuing the step. The wear is produced by straight and twisting slippage of leather or rubber over floor surfaces in conjunction with grit.

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[1] Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Atlanta, Ga., Feb., 1926. (White Wares Division.) Recd. Dec. 6, 1925.

[2] Industrial Fellow, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

The essential factors involved in working out a satisfactory abrasion test are as follows: (1) the conditions of wear must be similar to those in service; (2) leather or rubber must be used as a rubbing medium; (3) the abrasive grit must be loose and clean; (4) both the rubbing material and sample must be constantly cleaned to avoid contamination; (5) the degree of slippage must not be excessive; (6) the pressure exerted on the material must be similar to that applied to floors in service; (7) impact shocks must not be excessive or produced through other materials than those commonly used in shoes; (8) excessive heat must be avoided, and (9) the samples must be kept dry.

Other Abrasion Methods

It is pertinent to describe briefly some of the abrasion methods used by other investigators and point out their shortcomings for this particular research, wherein materials of widely varying physical properties were to be tested.

1. Sand Blast and Falling Abrasives

The wear produced by the use of sand blasts and falling abrasives is caused entirely by impact forces.

2. Fixed Sample Whirled in Loose Abrasives

The ratio of speed to the pressure exerted, when using the method of whirling a fixed sample in a bath of loose abrasive material, is not in the same proportion as that governing the wear in service; greatly increased temperatures are also evident.

3. Rattler Test

The rattler test produces wear mainly by impact forces. The variation in densities of materials causes different wearing effects.

4. Fixed Abrasive Wheel

The use of a fixed abrasive wheel to produce constant wear is a failure because the cutting edges change and the interstices between the abrasive particles fill with the worn material.

5. Rubbing against Hard Materials with Loose Abrasive

The use of rubbing mediums which are harder than the leather or rubber used in service produces an excessive cutting action; therefore, the resultant wear is not comparable to that observed practically.

The methods mentioned fail when materials tested have different characteristics. It is probable that those abrasion methods which can be controlled are acceptable when testing materials having the same physical properties.

Apparatus and Method Used

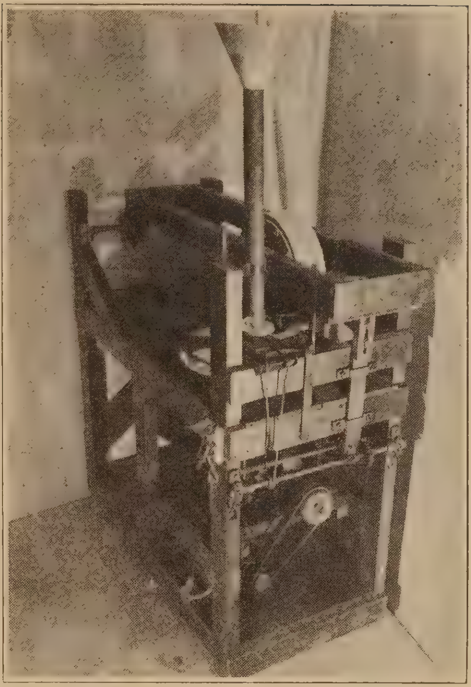

Fig. 1.—Abrasion machine used at Mellon Institute.

The apparatus shown in Figs. 1 and 2 was constructed to produce wear in compliance with the requisite factors as previously outlined. The wear is produced by an upright leather wheel rolling on a path of test samples placed on a horizontal revolving disk. Both wheels are driven in the same direction, but at slightly different speeds, by a positive-drive mechanism from a single power unit causing a constant slippage. A line perpendicular to the upright wheel from the point of contact lies two inches from the center of the horizontal disk. This arrangement produces a resultant outward motion, which also serves to constantly clean the samples and leather. The upright wheel is built of leather sections set on edge about its periphery. The best grade of oak tanned sole leather is used. The leather can be replaced without changing the wearing effect.

Two hundred grams per hour of a 60- to 80-mesh, crushed quartz sand is fed on the inside path of the samples by means of a special apparatus, which has a vertical reservoir cylinder placed on a horizontal revolving disk. The constant feeding depends on the flow of the sand through the adjusted opening between the cylinder and disk.

The lifting device is arranged to release the pressure at intervals in such a way that the effect progresses about the path of samples. The lift is adjusted every two hours to raise one-eighth inch above the samples. The test is terminated when the leather wheel has made 20,000 revolutions. The leather wheel is dressed to a true surface before each test, and is rebuilt whenever it has become worn so that its diameter is one inch less than originally.

Three-inch square samples of homogeneous floor coverings are prepared. Pliable materials are cemented securely to rigid aluminum plates. The triangular separating segments are of the same materials as the samples following them. Groups of tiles, cements, marbles, oxychloride cements, asphalts, woods, rubbers, and linoleums are tested each time. The samples, which are approximately one-half inch thick, are placed in the groove of the horizontal disk so that their exposed surfaces are of equal height. The weight or thickness losses of the flooring materials are noted and calculated to the percentage basis. Consideration has not been given to testing the resistance to abrasion of paint films or of surface dressings.

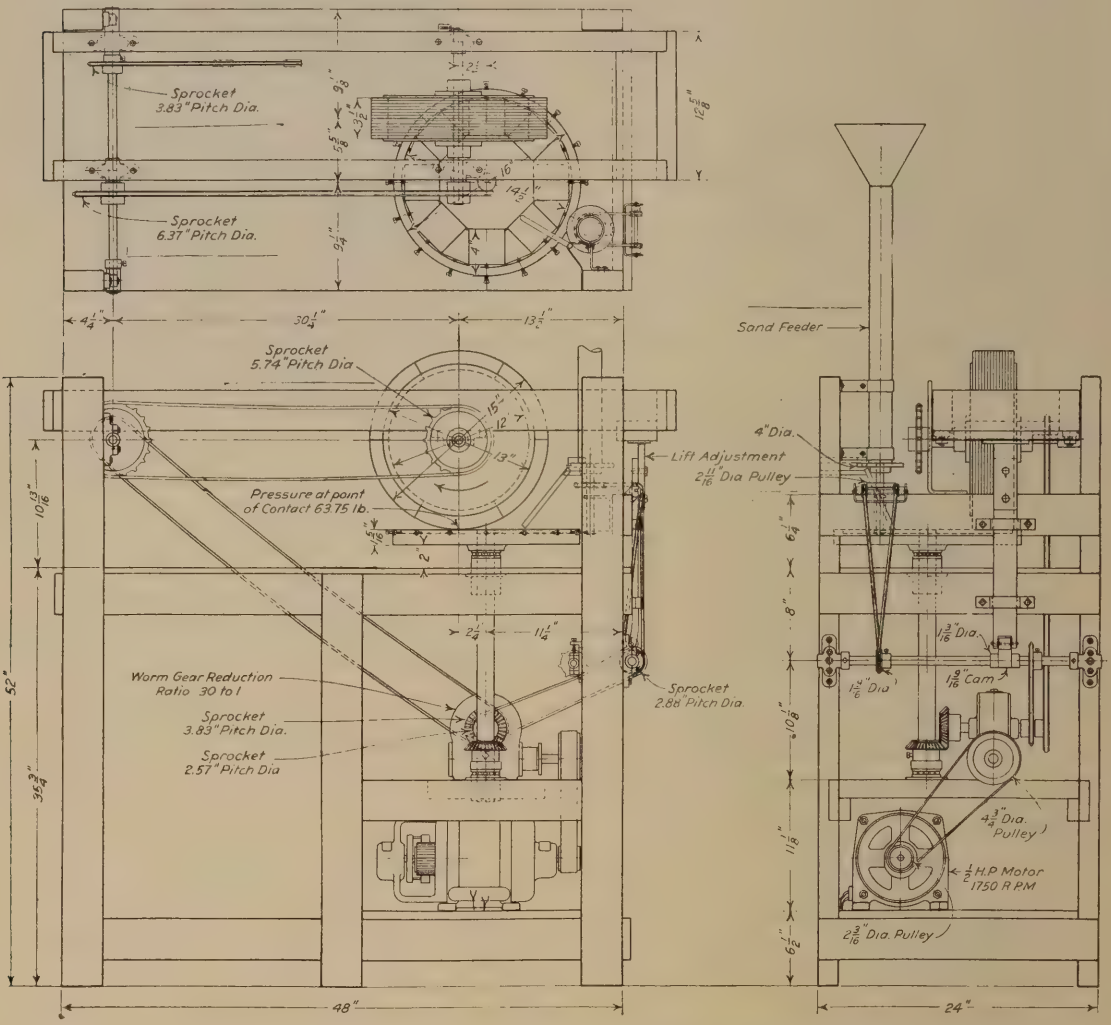

FIG. 2.—Details of construction of abrasion machine used at Mellon Institute.

Accuracy of Test Method

The results obtained in a series of tests on individual trade materials of different types are given in Table I.

TABLE I

VARIATION OF RESULTS FROM TESTS ON DIFFERENT MATERIALS

Material	Test 1 Per cent loss average 2 samples	Test 2 Per cent loss average 2 samples	Test 3 Per cent loss average 2 samples	Test 4 Per cent loss average 2 samples	Average Per cent loss	Maximum Per cent variation from average
Vitreous tile	4.65	4.39	4.69	4.56	4.57	3.93
Marble	22.88	23.23	23.49	22.73	23.18	1.94
Maple wood	24.18	24.33	23.27	23.39	23.79	2.27
Rubber	20.64	19.34	22.28	20.09	20.59	8.21
Linoleum	54.47	56.12	61.07	54.64	56.57	7.95
Oxychloride cement	53.17	49.03	50.92	47.30	50.10	6.12
Neat Portland cement	17.95	15.31	18.83	15.07	16.79	10.24
Asphaltic composition	78.05	88.01	80.63	73.76	80.11	9.86
Cork tile	46.02	44.86	42.63	50.20	45.93	9.29

The accuracy of the method is acceptable in view of the possible varying of materials and the accelerated wear. The factors governing the abrasion are similar to those in service. The results are logical and compare favorably with those generally expected of materials in service.

ENDURANCE OF FLOORING MATERIALS[1]

By Carl H. Geister[2]

ABSTRACT

The findings of a practical investigation of flooring materials are summarized. The endurance and sanitary properties of the materials were determined by use of the abrasion, absorption, indentation, chemical, stain, and age tests. The methods used are described.

Introduction

The endurant and sanitary properties of floor tile and of other floor coverings are being investigated at Mellon Institute. These qualities, which are considered of major importance in ascertaining the serviceability of flooring materials, are evaluated by determining the resistance of the materials to abrasion, absorption, indentation, chemicals, stains and deterioration from age. The test methods used as well as the results obtained thus far will be summarized in this paper. The requisite properties of floor materials and the practical conditions under which they are impaired have been discussed in several papers presented by the writer before the American Hospital Association.[3]

Methods of Test

For the purpose of determining the physical properties of materials in this investigation, in the light of the requirements of the study, it has been necessary to standardize certain test methods which will be of interest and applicable in problems of similar nature.

1. Abrasion An abrasion machine was built which was designed so that it is capable of closely imitating the wear produced on floors in service. Straight and twisting slippages as well as a stepping effect are produced. Pressure equal to that caused by the average person is applied to the sample by a leather rubbing surface, which in conjunction with siliceous grit affects the wear. The wear is produced without excessive temperatures or contamination of the leather and flooring material. A detailed description of the machine and method is given in the writer's paper, "An Accelerated Abrasion Test."[4]

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb. 1926. (White Wares Division). Recd. Dec. 6, 1925.

[2] Industrial Fellow, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

[3] "Adaptability of Tile to Hospital Requirements," presented before the American Hospital Association, Buffalo, N. Y., October 9, 1924; published in *Modern Hospital*, **23** [6], 575 (1924), and in *Hospital Buyer*, **3** [1], 16 (1924).
"Condition of Floors after Continued Service," presented before the American Hospital Association, Louisville, Ky., October 22, 1925.

[4] See preceding paper, *This Jour.*

2. Absorption

A method, which is in accordance with that prescribed in the Navy Department's specifications (29 L1C of September 1, 1916), was used in measuring the porosity of floor coverings. Only the homogeneous parts of the materials are considered, since surface dressings are not consistently used or are worn off shortly after application, and the various backings are not directly subjected to absorption.

The sublayers of cement, burlap or felt are removed. Samples weighing approximately fifty grams are prepared, which are dried and weighed. They are placed in water, kept at a temperature of 70°F, and removed for weighing when 24-, 48-, and 120-hour periods have elapsed. The adhering surface moisture is carefully blotted or wiped off, a period of two minutes being allowed for the blotting and weighing operations. The percentage increases are calculated from the following formula:

$$\frac{\text{Weight increase}}{\text{Original weight}} \times 100 = \text{percentage increase.}$$

3. Indentation

An apparatus was constructed in which a definite load can be applied to the caster that is fastened to a vertical shaft and rests on the sample. Tests were made in which loads varying from seventy-five to one hundred pounds were applied to casters ranging from one to three inches in diameter. The duration of the test was also varied. The effects caused by casters having steel, wood, felt or rubber wheels were studied. It was found that results obtained by the use of a one-inch steel caster under a load of seventy-five pounds for forty-eight hours are applicable in measuring resistances to depressions or pits caused by concentrated loads. The depressions after seven days' rest are of a permanent character. The percentage depths of depressions are calculated from the formula:

$$\frac{\text{Depth depression}}{\text{Original thickness}} \times 100 = \text{percentage depth depression.}$$

4. Chemicals

Only the homogeneous parts of materials are considered, as in the absorption test. The resistances of the materials to the following chemicals are determined:

Per cent
(*a*) 10 sodium bicarbonate
(*b*) 5 phenol
(*c*) 35 nitric acid
(*d*) 35 hydrochloric acid
(*e*) 50 sulphuric acid
(*f*) 15 acetic acid

Per cent
(*g*) 10 oxalic acid
(*h*) 50 sodium hydroxide
(*i*) 5 tincture of iodine
(*j*) 5 potassium permanganate
(*k*) 4 sodium hypochlorite

Samples weighing approximately ten grams are prepared, dried and weighed. They are submerged in the chemicals for twenty-four hours, removed and washed thoroughly or until the supernatant liquor does not show presence of the chemical after standing six hours. The samples are dried and weighed, and the percentage weight losses calculated.

After noting the visible physical changes, deterioration values are estimated. The changes in hardness are measured by means of the durometer apparatus. The physical changes and percentage losses are combined equally to determine the total deterioration values.

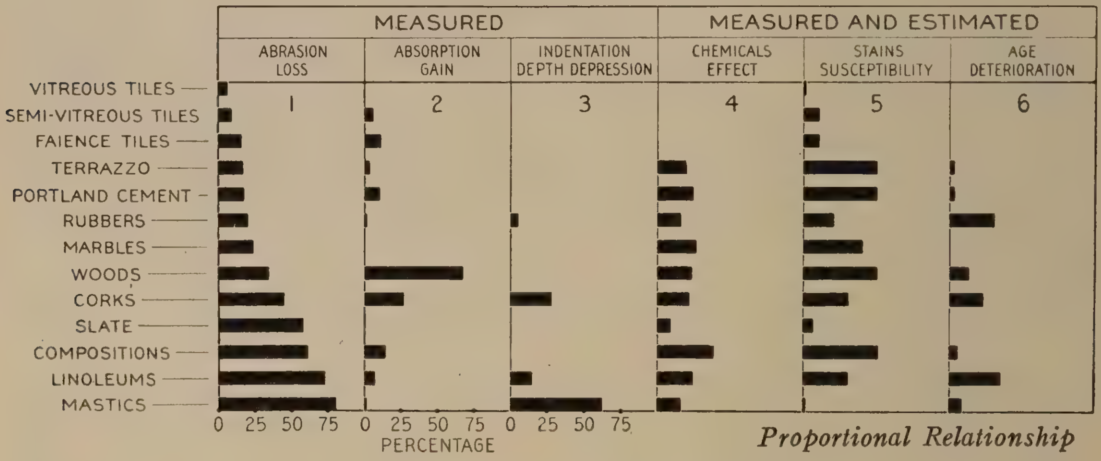

FIG. 1.—Summary of tests on flooring materials.

1. Per cent losses resulting from 20,000 revolutions of the leather wheel.
2. Per cent weight increases resulting from five days in water.
3. Per cent depth depressions after forty-eight hours under a one-inch caster, bearing a load of 75 pounds.
4. Composite values of per cent weight losses and estimated physical changes when treated with sulphuric, nitric, hydrochloric, carbolic, acetic and oxalic acids, and sodium hydroxide, sodium carbonate, iodine and potassium permanganate.
5. Composite values based on depths of penetration and degree of staining when treated with eosin, methylene blue, iodine and potassium permanganate.
6. Composite values of deteriorations resulting from water, warmth, sunlight, and alkaline soap powders.

5. Stains Samples measuring approximately 1 x 2 inches are prepared, dried and placed in 5% solutions of methylene blue, eosin, iodine and potassium permanganate. The samples are removed and rinsed after twenty-four hours have elapsed. The depths of penetration are measured, and consideration is also given to the degree of surface stains, physical changes, removal of stains, and resistance of the materials to chemical reagents. These five considerations are combined equally in determining the susceptibility of materials to stains.

6. Age The resistance of materials to deterioration from age caused by moisture, heat, sunlight and alkaline soap powder is found. The materials are soaked in water for four months; their weight losses

TABLE I

SUMMARY OF RESULTS FROM TESTING A REPRESENTATIVE NUMBER OF EACH MATERIAL

Type of Material	Thickness of Samples, Inches[1]	Abrasion Test, Per cent Loss 20,000 Revolutions	Absorption Test, Per cent Gain 5 Days	Indentation Test, Per cent Depth Depression[2]	Chemicals, Effect of, Measured and Estimated[3]	Stains, Susceptibility Measured and Estimated[4]	Age Deterioration Measured and Estimated[5]
Vitreous tiles	½	4.5	0.0	0.0	0.0-*A*	*A*	*AAAA*
Semi-vitreous tiles	½	8.6	5.1	0.0	0.0-*A*	*B*	*AAAA*
Faience tiles	½	15.3	10.6	0.0	0.0-*A*	*B*	*AAAA*
Terrazzo	½	16.1	2.6	0.0	11.4-*D*	*F*	*AAAB*
Portland cement	½	16.8	9.6	0.0	16.7-*D*	*F*	*AAAB*
Rubbers	¼	19.8	1.1	4.0	10.5-*C*	*C*	*EDBE*
Marbles	⅞	23.3	0.1	0.0	22.2-*D*	*E*	*AAAA*
Woods	½	33.8	66.1	0.0	15.2-*D*	*F*	*AACD*
Corks	½	44.2	25.5	26.7	12.4-*D*	*D*	*BAEE*
Slate	⅞	58.2	0.3	0.0	6.0-*B*	*AB*	*AAAA*
Oxychloride cements	½	60.4	13.1	0.0	34.5-*E*	*F*	*AABB*
Linoleums	⅛ and ¼	72.9	6.2	13.6	16.5-*D*	*D*	*EBEF*
Asphaltic compositions	¼ and ½	80.1	0.8	61.9	21.0-*B*	*A*	*CAAB*

[1] All samples were 3 inches square.

[2] Percentage depth depressions caused by a 1 inch caster under a load of 75 pounds for 48 hours.

[3] Percentage weight losses and estimated physical changes.
The letter *A* represents the minimum change.

[4] Combined values of depths of penetration, estimated degree of surface stains, and observed ease of removal.
The letter *A* represents the minimum susceptibility to stains.

[5] Deterioration values based on weight losses, hardening, rotting, fading, blistering, checking and swelling caused respectively by warmth, sunlight, moisture and alkaline soap powders. The letter *A* represents minimum deterioration.

and hardness changes are measured; the tendencies to fade, swell or decay are noted.

Samples are placed in an oven and kept at a temperature of 60°C for three months. The weight and hardness changes are measured, and the visible physical changes, as blistering and cracking, noted. Consideration is also given to the resulting odors.

The materials are subjected to sunlight for four months. They are protected from moisture by glass, which does not wholly remove the damaging effect of the sun. The hardness and physical changes, such as checking and fading, are observed.

The materials are placed in a 10% (by weight) soap powder solution which is kept at a temperature of 60°C. The weight losses and hardness changes are measured, and the degree of swelling, fading and decaying of materials estimated. The resistances of materials to moisture, heat, sunlight and alkaline soap powders are considered.

Experimental Results

The physical properties studied are presented concisely in Fig. 1, which is based on the results given in Table I.

Conclusions

The methods discussed are applicable for determining practically the behavior of flooring materials in service with special attention to their durability and hygienic aspects. It has been shown that tiles have maximum endurant properties and greatly assist in producing sanitary conditions. Tiles are fireproof, which quality is endorsed by their general use in fireplace construction. They are inodorous, resistant to abrasion, moisture, chemicals and stains, and do not deteriorate with age.

PROGRESS REPORT ON INVESTIGATION OF SAGGER CLAYS[1]

By R. A. Heindl

ABSTRACT

This paper is the first progress report of a comprehensive study of sagger clays. It includes the results of a preliminary study of clays representative of those used in sagger making throughout the United States. Chemical analyses, and a summary of physical tests, petrographic examinations, and the effect of repeated burns in pottery kilns are given. As a result of this work the clays have been classified into five groups characterized by properties in the fired state. The paper also contains an outline of a proposed intensive and fundamental study of a limited number of clays typical of each group.

Introduction

The uses and limitations of saggers, their shapes and sizes, the methods of their manufacture, and the raw materials used, have been discussed at great length in ceramic literature.[2] While much of the information contained in the articles referred to is elementary, the specific data are usually based on results of long and painstaking investigations. This is no doubt enabling the potter to produce better saggers, but the breakage is still high and causing a loss of millions of dollars annually.[3] To assist the industry in eliminating this waste, the Bureau of Standards, in coöperation with the United States Potters Association, undertook a comprehensive investigation of sagger clays. While it is the ultimate purpose of this work to obtain a better understanding of all the factors controlling the life of saggers, the first phase of the investigation is being confined to a study of the characteristics of the individual clays.

Scope

Samples of fifty-one different clays, representing as well as could be judged, all the important clay mining districts of the country, were included in the investigation. Four-hundred pound samples of each clay were obtained from the consumer whenever possible, rather than from the producer, in order that experimental results might represent the properties of clays as actually used in the plant.

In order to classify the sagger clays according to their properties, the following determinations were made: (1) water of plasticity; (2) volume and linear shrinkage; (3) porosity and modulus of rupture in the dry state; (4) softening point; (5) strength, porosity and shrinkage after firing at five different temperatures; (6) resistance to dunting; (7) petrographic examination and chemical analyses.

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[1] Published by permission of the Director of the Bureau of Standards of the U.S Department of Commerce. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (White Wares Division.) Received December, 1925.

[2] *Transactions* and *Journals of the American Ceramic Society*. "Clays, Occurrence, Properties and Uses," by H. Ries. "The Chemistry and Physics of Clays and Other Ceramic Materials" (1924), and "Refractory Materials, Their Manufacture and Uses," 2d Ed. (1924), p. 442 by A. B. Searle.

[3] *Bull. Amer. Ceram. Soc.*, 1 [3], 103 (1923).

Methods of Testing and Results

Unfired Clays Saggers used in industrial practice contain a large percentage of variously sized grog. To simulate this condition and to facilitate proper drying of the bodies, test bars 1x1x7 inches were made consisting of 50% clay and 50% of sized grog. The grog used was made in each case from the clay with which it was to be bonded, thereby eliminating any factors which might influence the properties of the individual clay due to admixed clay, or clays. In preparing the grog, the clay was well pugged, fired at 1200°C for one and one-half hours,[1] cooled, crushed and screened. Thirty per cent of the grog used in all test specimens passed a No. 20 and was retained on a No. 40-sieve, and 70% passed a No. 40-sieve.

Water of Plasticity The water of plasticity was determined according to the standard AMERICAN CERAMIC SOCIETY method except that the results were calculated as a percentage of the plastic instead of the dry weight. The water of plasticity ranged from 13.7 to 31.7%, with an average of 19.5%; 92% of the clays had sufficiently good working qualities so that they could be used satisfactorily for the purpose intended.

Volume Drying Shrinkage The volume drying shrinkage was determined according to the standard AMERICAN CERAMIC SOCIETY method for shrinkage water except that the results were calculated as a percentage of the plastic rather than the dry volume. The shrinkage ranged from 9.1 to 16.9%, with an average of 13.1%.

Linear Drying Shrinkage The linear drying shrinkage was measured on the briquets which were prepared for the fired-strength tests. The lowest linear drying shrinkage was 2.8%, the highest 6.1%, and the average 4.5%.

Porosity The porosity was calculated in accordance with the following formula:

$$P = \frac{S-D}{Vd} \cdot 100$$

P = percentage porosity
D = weight of test piece after having been dried at 110°C to constant weight
S = weight of test piece saturated with kerosene
V = volume of dry test piece
d = density of kerosene

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[1] This heat treatment was used in order to produce a grog which was sufficiently fired to have the requisite mechanical strength and still porous enough to bond well with the raw clay.

The volume of the dried briquet which had been used for the water-of-plasticity test, was determined as follows: The clay specimen was completely immersed in kerosene for two and one-half hours at an absolute pressure of four millimeters of mercury. The saturated test piece was then taken from the bath, wiped lightly with a cloth to remove excess kerosene, and weighed in air to the nearest 0.1 gram. The weight of the briquet suspended in kerosene was also determined. The difference between these two weights divided by the density of the kerosene gave the volume of the specimen. The average of determinations on three specimen bars 1x1x2 inches was considered representative. The porosity ranged from 24.4 to 50% and the average was 31.9%.

Modulus of Rupture For the determination of dry modulus of rupture, clay bars 1x1x7 inches were dried for ten days at room temperature, 24 hours at 50°C, and finally 24 hours at 110°C. The linear measurements were made to the nearest $\frac{1}{1000}$ inch.

The moduli of rupture varied from 46 pounds per square inch for the slightly plastic clays to 386 pounds per square inch for a clay of superior plasticity. The average modulus of rupture was 221 pounds per square inch. All of the clays which had relatively poor plasticity showed a modulus of rupture of less than 100 pounds per square inch, while over 75% of the remaining clays showed a modulus of rupture of 200 or more pounds per square inch. No close relation appears to exist between porosity and modulus of rupture, although in those samples showing relatively little plasticity the porosity is generally high.

Softening Point The softening points were determined in an electrically heated muffle,[1] by comparison with Orton pyrometric cones. The heating schedule followed is approximately that prescribed in the A.S.T.M. Standard Method of Test for Softening Point, Serial Designation C 24–20.

The lowest softening point was found to be cone 14+; in general the determinations indicate that the majority of the clays are of good refractory quality.

According to softening points, the 51 clays may be classified into four groups, as follows:

Group 1	Sixteen clays having a softening point equivalent to or above that of cone 31.
Group 2	Nineteen clays having a softening point ranging from cones 28 to 30 inclusive.
Group 3	Twelve clays having a softening point ranging from cones 20 to 27 inclusive.
Group 4	Four clays having a softening point equal to or below cone 19.

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[1] W. L. Pendergast, "Electric Furnace for Softening Point Determinations," *Jour. Amer. Ceram. Soc.*, **8** [5], 319 (1925).

Chemical Composition The chemical analyses of the unfired clays (Table I) consisted of the routine determination of ignition loss, SiO_2, Al_2O_3, Fe_2O_3 and TiO_2. Other constituents were not determined, but the difference between 100% and the sum of the percentages of ignition loss, SiO_2 and Al_2O_3 was regarded as the

TABLE I

CHEMICAL COMPOSITION OF SAGGER CLAYS

Clay	Loss on ignition	SiO_2	Fe_2O_3	TiO_2	Al_2O_3	Other flux (by difference)
1	8.5	63.6	1.5	1.3	21.9	3.2
2	9.8	61.4	1.6	1.6	24.8	0.8
3	6.0	73.4	1.3	1.3	17.0	1.0
4	11.3	50.5	3.8	1.2	31.3	1.9
5	9.9	58.3	1.2	1.1	27.9	1.7
6	14.8	43.7	0.9	1.7	38.7	0.2
7	11.8	51.4	3.0	1.2	30.8	1.8
8	10.9	52.6	3.9	1.2	29.8	1.6
9	12.9	46.8	0.9	2.0	35.9	1.5
10	8.5	65.3	1.1	1.3	23.1	0.7
11	14.5	42.9	1.8	2.5	37.9	0.4
12	10.7	54.7	1.3	1.6	29.8	1.9
13	10.7	66.1	0.6	1.2	20.0	1.4
14	13.9	51.8	1.0	1.6	29.5	2.2
15	7.3	64.1	1.5	1.1	22.7	3.3
16	14.1	42.4	0.5	1.3	39.5	2.2
17	12.3	50.4	3.4	1.0	31.4	1.5
18	9.5	56.8	0.9	1.1	30.0	1.7
19	7.6	66.1	0.5	0.8	24.9	0.1
20	8.4	66.1	1.2	1.0	23.2	1.0
21	8.3	60.9	2.0	1.1	26.5	1.2
22	11.1	58.1	0.7	1.0	27.0	2.1
23	6.8	68.5	1.0	1.4	19.3	3.0
24	10.6	56.4	0.6	1.3	29.9	1.2
25	14.0	47.1	0.5	2.5	35.0	0.9
26	8.2	63.8	1.0	1.1	23.1	2.8
27	12.6	57.3	1.5	2.1	25.5	1.0
28	9.8	57.5	2.1	1.6	26.2	2.8
29	8.9	64.9	1.7	1.5	21.3	1.7
30	11.1	55.5	1.9	2.0	28.7	0.8
31	12.7	48.9	1.0	1.7	30.9	4.8
32	8.4	60.6	2.1	1.0	24.3	3.6
33	11.6	53.6	0.9	2.2	30.9	0.8
34	8.1	62.6	0.9	1.5	25.0	1.9
35	8.0	61.6	1.5	1.6	23.5	3.8
36	7.7	56.8	1.8	1.5	26.5	5.7
37	7.0	58.1	3.0	1.0	25.8	5.1
38	7.7	62.1	1.7	1.6	23.3	3.6
39	11.6	54.9	1.3	1.6	28.0	2.6

TABLE I (*concluded*)

CHEMICAL COMPOSITION OF SAGGER CLAYS

Clay	Loss on ignition	SiO_2	Fe_2O_3	TiO_2	Al_2O_3	Other flux (by difference)
40	8.5	62.8	1.0	1.9	24.1	1.7
41	11.7	57.8	0.8	2.0	26.5	1.2
42	8.2	64.6	1.6	1.5	22.4	1.7
43	11.4	52.4	2.5	1.3	29.9	2.5
44	11.7	51.3	1.9	1.2	31.4	2.5
45	8.9	61.3	1.1	1.5	26.2	1.0
46	10.4	59.5	1.2	1.7	25.7	1.5
47	13.4	55.4	3.6	1.3	23.5	2.8
48	10.2	58.5	1.2	1.6	26.5	2.0
49	15.0	49.0	1.5	1.7	32.0	0.8
50	10.9	54.8	1.1	1.8	30.5	0.9
51	10.5	60.2	1.5	1.0	23.7	3.1

percentage of flux. The clays show a wide variation in composition, as indicated by the range in SiO_2 from 49 to 78%, Al_2O_3 from 18 to 46%, and the total flux from 1.5 to 10%.

Rational Composition vs. Softening Point The rational composition[1] calculated from the chemical analyses, shows that the clay content varies from 43 to 95%, the uncombined quartz from 4 to 53% (except for three clays which show a small excess of Al_2O_3), and the total flux from 1 to 9%. Only four of the clays have uncombined quartz in excess of 40%, 15 clays have uncombined quartz in amounts ranging from 30 to 40%, for 15 clays it varies between 20 to 29%, and the balance have less than 20%.

It is interesting to note that the softening point varies inversely as the ratio of average flux content to the clay content in each of the four groups into which the clays have been classified according to softening point (Table II).

TABLE II

Grouped according to softening points (in cones)	*a* Average clay content	*b* Average flux content	Ratio $\frac{b}{a}$
31 or higher	92.0	4.5	.049
28–31, inc.	75.7	4.6	.061
20–27, inc.	63.9	5.0	.078
Below 19	66.7	6.7	.100

Fired Clays Ten bars 1 x 1 x 7 inches, made of a composition of each clay and grog as described under testing of unfired clays, were subjected to each of five firings ranging in temperature from 1150°C to 1310°C (cones 3 to 12) with an interval of 40° between succeeding firings. (Exceptions: the firing scheduled to be made at 1190°C was made at 1180°C and three clays, the softening points of which proved to be around cone 15 and which consequently overfired at 1270°C, were fired at 1110°C as the minimum temperature instead of 1150°C). The maximum temperature was held in each firing for one and one-half hours to insure equilibrium in the clay for that temperature.

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[1] U.S. Bur. Stand., *Tech. Paper*, 279, p. 126.

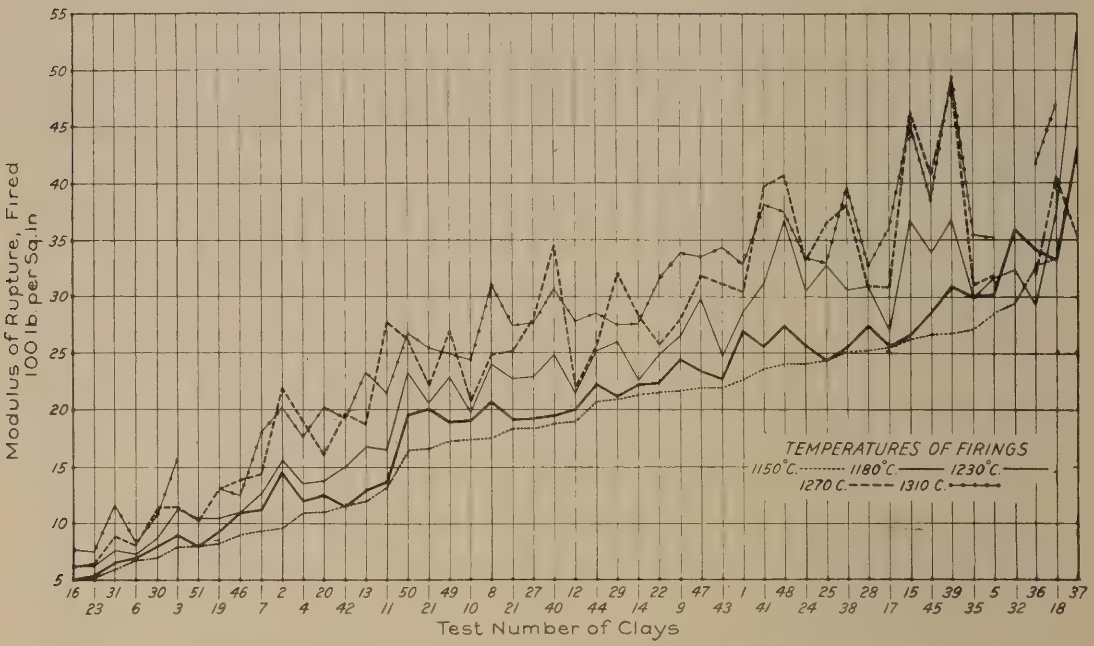

FIG. 1.—Shows that 15 clays had reached their highest transverse strength during the 1270°C firing, and 33 clays showed greater strength after being fired at 1310°C although the porosity and volume shrinkage indicate the latter to be overfired at this temperature (Fig. 2).

Modulus of Rupture The results of tests for modulus of rupture are shown in Fig. 1 and summarized in Table III.

TABLE III

RANGE IN MODULUS OF RUPTURE (LBS./IN.²)

Firing °C	Min.	Max.	Av.
1110	405	3850	2600*
1150	500	4340	1880
1180	510	4340	2030
1230	620	5350	2320
1270	610	4850	2590
1310	755	4960	2760

* Average on three clays only.

Figure 1 shows that 15 clays had reached their highest transverse strength during the 1270°C firing, and 33 clays showed greater strength after being fired at 1310°C although the porosity and volume shrinkage indicate the latter to be overfired at this temperature (Fig. 2).

Porosity and Volume Shrinkage The results of the porosity and volume shrinkage determinations are shown in Fig. 2 and summarized in Table IV.

TABLE IV

RANGE IN POROSITY AND VOLUME SHRINKAGE (PER CENT)

	Porosity			Volume Shrinkage		
Firing °C	Min.	Max.	Av.	Min.	Max.	Av.
1110	18.0	23.5	19.9	2.2	14.9	10.0
1150	17.4	46.5	31.1	1.9	16.3	7.6
1180	13.9	45.9	30.8	2.7	18.2	8.3
1230	8.1	40.8	27.1	4.0	24.7	11.0
1270	1.0	38.5	22.5	2.1	35.7	14.3
1310	8.8	39.2	25.0	2.5	30.2	11.0

The greatest change in porosity in all the clays (clay 15) was from 27.5 to 3.4%; the smallest change (clay 3) was from 33.5 to 31.2%. The greatest change in volume shrinkage (clay 8) was from 7.9 to 26.3%; and the smallest change (clay 20) was from 4.1 to 5.3%. The curves (Figs. 2 and 3) representing the results obtained by firing the clays at 1310°C, the highest temperature used, clearly show that all clays were overfired.

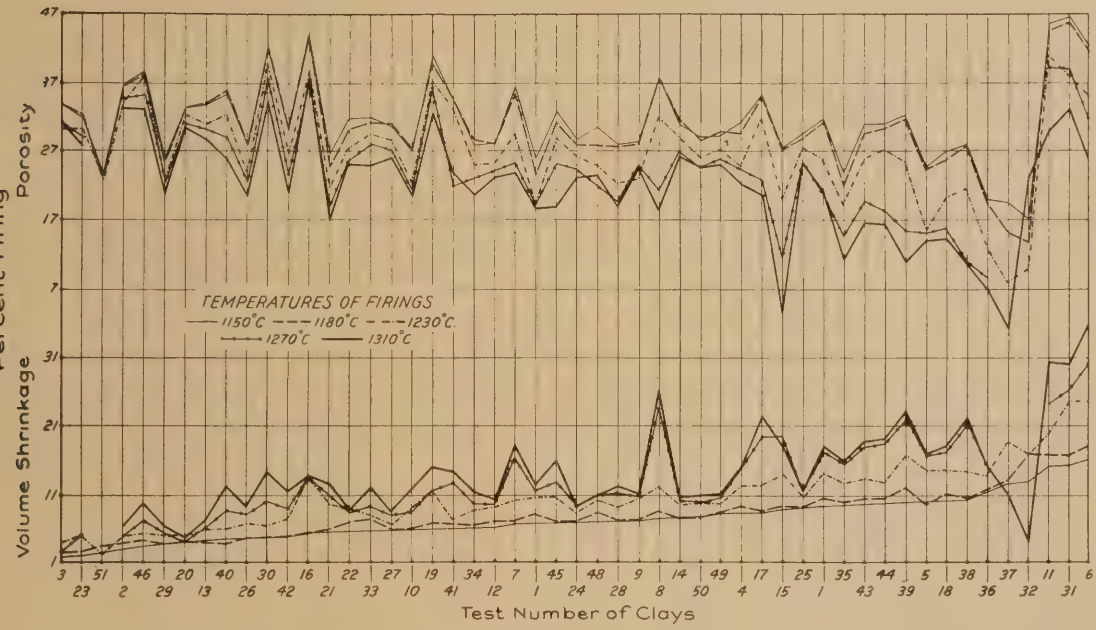

FIG. 2.

Petrographic Examinations Fifteen clays, fired to the five temperatures mentioned above, were examined petrographically. It was noted that the formation of glass and the crystallization of mullite increased with increasing temperatures, and that the presence of glass (due to fluxing impurities) facilitated the growth of mullite crystals. However, it is now a matter of fairly common knowledge that these reactions take place in all clays when subjected to high temperatures.

Air Quenching or Dunting Tests

Small, oval saggers, 4x4x6x½ inches, were made for the quenching test, in order to simulate the strains developed in commercial saggers. No attempt was made to build an ideal sagger, the object being to obtain a relation between the ability to withstand thermal shock and the nature of the clay. Ten specimen saggers of each clay, made of a composition of 50% grog and 50% clay as described in preceding tests and fired to 1240°C (cones 8½ to 9½), were subjected to the following quenching tests:

(*A*) Five saggers of each clay, at room temperature, were placed in a furnace held at 575°C and allowed to remain there for one-half hour before being quickly withdrawn and permitted to stand in the air. These saggers were subjected to this thermal shock test until fractured, or until a maximum of 30 tests had been made if not fractured before reaching that number.

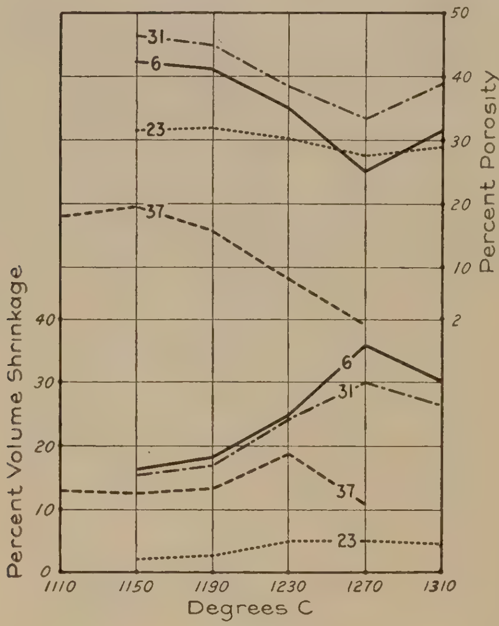

FIG. 3.

This experiment was not productive of good comparative results since the majority of saggers fractured during the first test. Only five clays withstood the maximum number of shocks and a sixth, although showing no fracture, did not ring when struck and undoubtedly contained invisible cracks.

(*B*) The second five saggers of each clay were air-quenched from progressively higher temperatures until fracture occurred. The initial furnace temperature was 350°C, the second 400°C, and each succeeding temperature was increased 25°C until 800°C was reached. The test conducted in this manner gave a satisfactory series of comparative results, although the majority of saggers fractured below or at 575°C. Saggers made of one clay, which is undoubtedly a bauxitic clay[1] were still apparently perfect at 1000°C.

In view of the discoveries of Peters,[2] Norton[3] and Booze[4] it is not surprising that no definite relation was found to exist between the relative resistance to failure in the thermal shock test with the physical characteristics of the raw and fired clays or with their chemical composition. Norton and Booze have demonstrated that flexibility in shear, diffusivity, and coefficient of expansion are factors which should be considered in studying the life of refractories in service. Furthermore, Endell[1] has obtained data indicating that variations in expansivity, or thermal dilatation, may be brought about not only by varying the percentages of quartz, and its allotropic forms, but also by varying the fineness of grain. That is, quartz added as coarse crushed ganister may produce a change in expansion entirely different than that caused by an equal quantity present as an exceedingly fine-grained and inherent component of the clay.

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[1] Approximate composition; Al_2O_3 40%, SiO_2 42%, flux 3%, ignition loss 15%.

[2] M. F. Peters, *Jour. Amer. Ceram. Soc.*, **5**, 181 (1922).

[3] F. H. Norton, *Jour. Amer. Ceram. Soc.*, **8** [1], 29 (1925).

[4] M. C. Booze and S. M. Phelps, *Jour. Amer. Ceram. Soc.*, **8** [6], 361 (1925).

A sagger body should be of a good plastic consistency and the sagger in the unfired state must possess reasonable strength and satisfactory drying properties. Therefore, determinations of the water of plasticity, drying shrinkage, porosity and dry modulus of rupture are valuable. Fired saggers must have high mechanical strength to withstand the stresses and shocks incident to handling, and the loads imposed in use; they should have as high a porosity as possible, consistent with strength and thermal diffusivity, in order to withstand thermal shocks; and they should have a relatively low shrinkage in the initial firing to minimize strains and cracks before their full strength is attained. Therefore, determinations of the shrinkage, porosity and strength of the fired clays are valuable. Nevertheless, as is evident from a consideration of the results obtained by these investigators, a satisfactory understanding of the factors controlling the life of saggers in service necessitates a more profound study than the carrying out of such conventional tests as have been described above.

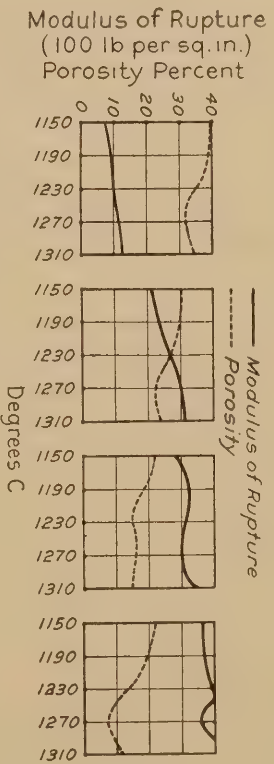

FIG. 4.

In addition to determinations of expansivity, diffusivity, and elasticity, it would also be desirable to study the effect of varying the firing treatment and sizing of the grog. Such an intensive study of each of the 51 clays under consideration, or of even a very small number of the possible combinations of these clays, would be impracticable. Therefore, it was essential to classify or group the clays in order that two or three from each group might be chosen for further study and be logically considered as typical of all the rest.

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[1] Berichte der Fachauschüsse des Vereins deutscher Eisenhüttenleute (No. 52) October 10, 1924.

Grouping of Clays

As the highest temperature at which saggers are used is far below the softening point of the average sagger clay, it is obvious that other properties such as strength, porosity or resistance to fracture due to thermal shock are of greater importance than its ultimate refractoriness. It is for this reason that the clays were grouped in the order of increasing average modulus of rupture and decreasing average porosity, as illustrated in Figs. 4 and 5 and tabulated in Table V. Groups *A*, *B*, and *C* are composed of clays with

Table V

Grouping According to Properties of Fired Clay

		Fired at				
Clay Numbers		1150°C	1180°C	1230°C	1270°C	1310°C
Group *A* 2, 3, 6, 7, 16, 19, 23, 30, 31, 46.	Modulus of rupture lbs./in.^{2}	740	870	970	1160	1250
	Porosity per cent	39.2	39.0	35.2	31.5	34.0
Group *B* 1, 8, 9, 10, 12, 14, 21, 22, 24, 25, 26, 27, 29, 40, 41, 43, 44, 47, 48, 49, 50.	Modulus of rupture lbs./in.^{2}	2040	2220	2590	2930	3050
	Porosity per cent	30.0	29.7	26.5	22.2	23.7
Group *C* 5, 32, 35,	Modulus of rupture lbs./in.^{2}	2830	3210	3130	3020	3530*
	Porosity per cent	21.9	20.0	15.0	16.1	14.8
Group *D* 18, 36, 37,	Modulus of rupture lbs./in.^{2}	3650	3690	3970	3600	4420*
	Porosity per cent	22.1	20.4	13.9	7.6	12.2
Group *E* 15, 38, 39,	Modulus of rupture lbs./in.^{2}	2600	2770	3480	4420	4500
	Porosity per cent	29.3	29.0	22.5	9.3	12.6

* Average of two clays only in 1310°C firing.

satisfactory firing properties, group *D* might be considered fair, while group *E* contains clays with decidedly undesirable firing properties.

For convenience the values given in Table V are roughly summarized as follows:

Group	Modulus of Rupture Lbs./in.²	Porosity Per cent
A	Less than 1500	30–40
B	Between 1500–3000	23–30
C	Between 2800–3500	14–23
D	Between 3500–4500	7–23
E	Between 2500–4500	7–30

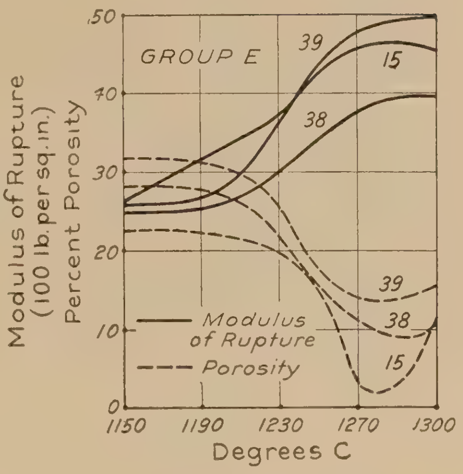

FIG. 5.

Supplementary Tests

In order to study progressive changes which may take place in sagger bodies in the course of successive firings, 125 bars were prepared, composed of 75% clay and 25% grog, of each of two clays and a mixture of the two in equal proportions, and a similar number of bars of each of three clays and a mixture of the three in equal proportions. These bars (representative of commercial sagger bodies) were then submitted to the Warwick China Company and the Crooksville China Company where they were placed in saggers with regular ware and subjected to repeated firings at cone 11 in one pottery, and at cone 9 in the other. Ten specimens of each clay or body were returned to the Bureau of Standards at the end of each firing for the first five consecutive firings and thereafter at intervals of three firings until the final specimens had received 17 firings by the one pottery and 26 firings by the other.

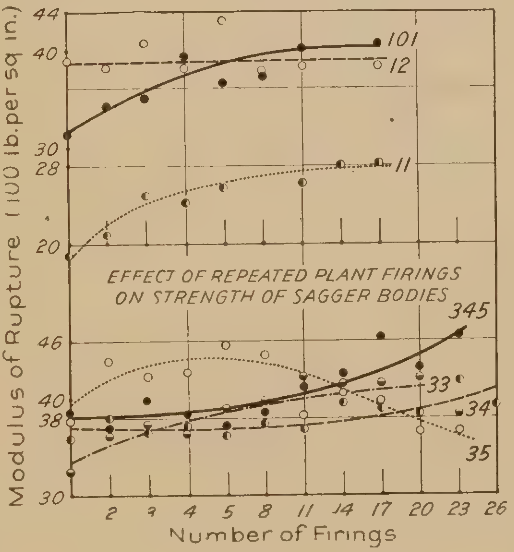

FIG. 6.

Progressive changes in physical properties due to repeated firings are given in Table VI, and the change in modulus of rupture is illustrated in Fig. 6. These may be summarized as follows:

Clay 11: marked increase in transverse strength and a decrease in porosity.

Clay 12: very little change in transverse strength, but a decided increase in porosity and a possible overfiring after 11 firings.

TABLE VI

SPECIMENS FIRED IN COMMERCIAL KILNS

Firing	Porosity in Per Cent Average on three specimens Clay Numbers						
	11	12	101	33	34	35	345
1	34.4	21.1	29.8	24.2	19.7	6.0	15.6
2	33.5	19.0	26.8	22.7	21.3	5.4	15.5
3	31.4	14.6	24.6	19.7	20.7	4.5	12.2
4	30.2	14.5	23.7	18.2	21.1	5.2	13.6
5	30.5	14.0	24.4	17.9	19.4	3.9	12.6
8	32.8	12.1	22.1	19.5	14.0	6.2	12.4
11	31.8	11.7	17.2	16.8	13.9	7.4	11.3
14	30.1	14.7	20.2	20.0	17.9	8.1	12.9
17	30.0	15.3	22.0	20.7	18.5	8.6	12.4
20	—	—	—	19.3	17.8	9.2	12.3
23	—	—	—	17.6	17.8	10.4	11.4
26	—	—	—	18.1	17.3	11.4	10.5

Firing	Volume Shrinkage in Per Cent Average on three specimens Clay Numbers						
	11	12	101	33	34	35	345
1	26.0	20.0	22.1	23.2	19.3	21.9	22.0
2	27.6	21.4	23.6	23.7	17.8	22.1	22.2
3	29.5	22.1	24.1	24.5	18.3	22.4	22.4
4	30.2	22.8	25.0	25.2	18.5	22.2	22.3
5	30.7	22.7	24.9	25.1	18.6	22.6	22.5
8	—	—	—	—	—	—	—
11	—	—	—	—	—	—	—
14	—	—	—	—	—	—	—
17	—	—	—	—	—	—	—
20	—	—	—	—	—	—	—
23	—	—	—	—	—	—	—
26	—	—	—	—	—	—	—

Firing	Modulus of Rupture (Lbs./sq. in.) Average on 8 to 10 specimens Clay Numbers						
	11	12	101	33	34	35	345
1	1890	3910	3150	3270	3610	3820	3820
2	2100	3820	3430	3650	3770	4410	3860
3	2520	4080	3520	3720	3670	4240	4010
4	2540	3810	3950	3670	3730	4280	3860
5	2570	4320	3680	3640	3680	4530	3810
8	3090	3780	3760	3920	3850	4450	3880
11	2650	3830	4020	4000	3710	3820	4140
14	2820	3410	3510	4240	3960	4060	4270
17	2830	3840	4090	4150	3960	3920	4650
20	—	—	—	4180	3870	3660	4340
23	—	—	—	4220	4200	3690	4660
26	—	—	—	3840	3970	—	4170

Clays 11, 12, 101 fired to cone 11.
Clays 33, 34, 35, 345 fired to cone 9.

Body 101: representing an equal mixture of clays 11 and 12; increase in transverse strength, a marked decrease in porosity and possible overfiring after 11 firings. The data indicate that fired specimens of this body had greater strength at the end of the test than fired specimens of either of the individual clays.

Clays 33 and 34: increasing transverse strength with a decrease in porosity.

Clay 35: overfired; after five firings a decrease in transverse strength and an increase in porosity indicating a short vitrification range.

Body 345: representing an equal mixture of clays 33, 34 and 35; increase in transverse strength and a decrease in porosity. The average modulus of rupture of fired specimens of this body is greater than that of fired specimens of any of the three individual clays.

The petrographic examination of body 345 showed incipient mullite needles at the end of the first firing. These became more pronounced with succeeding firings, and glass, present in considerable quantities in the first firing, also increased in the following firings. The petrographic examination of clay 33 showed progressive changes with repeated firings. The first trace of mullite appeared at the end of 11 firings, with a gradually increasing amount appearing with succeeding firings. A notable increase in glass content appeared in the specimen subjected to eight firings, with a gradually increasing amount appearing in succeeding firings, indicating the approach of complete vitrification.

Although mullite is formed in these clays by repeated firings, no conclusion has been reached relative to the effect of this crystal growth on the strength of the clays. However, the increase in the quantity of glass due to repeated firings undoubtedly increases the modulus of rupture when determined by breaking slowly cooled specimens, but very probably this increase in the quantity of glass causes a weakening of the structure under load at high temperatures, due to the glass being in a mobile state. Therefore, although the cold modulus of rupture is shown to be increased in these bodies by repeated firing, the structure at kiln temperatures may actually be weaker due to the greater content of glass.

Future Work

Having obtained sufficient data to group or classify the clays included in the investigation, it is now proposed to take, from each group (*A*, *B*, *C*, *D* and *E*), three clays having the highest, lowest and a medium resistance to failure in the dunting test and subject them to an intensive study.

It is hoped that the information gained from the work outlined will be sufficiently conclusive to warrant its application to plant practice.

THE DESIGN OF ARCHES FOR KILNS AND FURNACES[1]

By F. H. Norton[2]

ABSTRACT

The design of arches is considered from the view point of minimizing the static and temperature stresses. The catenary shape of arch is most satisfactory, as it allows the use of a high arch with good stability. Some actual designs are worked out to illustrate the method of calculating a catenary arch.

Introduction

The design of high temperature arches has not hitherto received as careful study as the usual masonry arch. There are a number of excellent treatises[3] on the latter type of arch but they are of little assistance because of the different construction in the two cases.

The masonry arch generally has a stiff spandrel backing and strong mortar joints so that the stability of the arch ring alone is not of primary importance. On the other hand the furnace arch is a relatively slender ring with no support except at the skewbacks, and the joints cannot be depended upon to take tension. This makes the computation of the static stresses quite simple, but the temperature stresses can only be approximated.

Static Stresses in Circular Arches

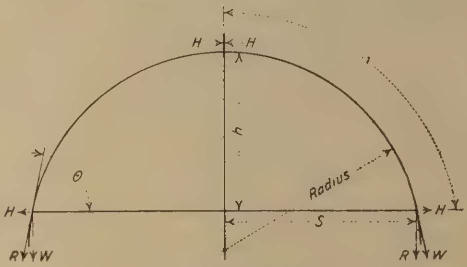

Fig. 1.—Circular arcs.

Let us first consider the mean stress over a unit section in a circular arch ring at the skewback and at the crown. Referring to Fig. 1, the load on the skewback, parallel to the direction of the ring, is;

$$R = w \operatorname{cosec} \theta \qquad (1)$$

and the compression at the crown is:

$$H = w \cot \theta \qquad (2)$$

where

θ = angle of ring with horizontal at skewback

w = weight of a slice of the arch one unit long and extending from the crown to the skewback, $= Wl$, where W equals the weight of a unit block taken in a plane tangent to the arch.

l = semi-arc,

h = rise,

s = semi-span.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlantic, Ga., Feb., 1926. (Glass-Refractories Symposium.) Recd. Nov. 17, 1925.

[2] Babcock and Wilcox Fellow, Division of Industrial Coöperation and Research, Massachusetts Institute of Technology.

[3] Baker, A Treatise on Masonry Construction.
Allan, Theory of Construction.
Howe, Symmetrical Masonry Arches.
Sondericker, Graphic Statics.

The increase in loads due to flattening the arch is shown in the following table:

TABLE I

$\frac{s}{h}$	l	w	θ	cosec θ	cot θ	R	H
1	1.57	1.57	90°	1.00	0.00	1.57	0.00
2	1.16	1.16	53	1.25	0.75	1.45	0.87
4	1.03	1.03	28	2.13	1.88	2.19	1.94
8	1.01	1.01	14.2	4.06	3.95	4.06	3.96
16	1.00	1.00	7.1	8.08	8.03	8.08	8.03
32	1.00	1.00	3.5	16.00	16.00	16.00	16.00

$s=1$ $w=1$

It will be noticed that R is a minimum when $\frac{s}{h}$ is about 1.8.

The average stresses have been considered above, but the stresses due to eccentric loading may be much larger, especially in the higher arches. The centers of thrust on the arch bricks will lie on a catenary curve when the crown is of uniform weight. By finding the difference between a circle and a catenary, the eccentricity and increased load can be determined. This has been worked out in the following table:

TABLE II

$\frac{s}{h}$	Difference between circle and, catenary at crown and skew-back in terms of s.	Stress factor when thickness of ring is		
		0.15	.055	.0255
1	0.045	2.35	unstable	unstable
2	0.030	1.90	2.80	unstable
4	0.005	1.15	1.30	1.60
8	0.000	1.00	1.00	1.00
16	0.000	1.00	1.00	1.00
32	0.000	1.00	1.00	1.00

$s=1$

The intensity of stress was computed from:

$$f=\frac{P}{A}(1+3\frac{d}{b}) \qquad (3)$$

where;

P = the average load

A = the unit area

d = is the distance of the load line from the neutral axis

$b=\frac{1}{2}$ the thickness of the ring

In Table II the factor $(1+3\frac{d}{b})$ is given to show how the loads in Table I are increasing in the higher arches by considering the eccentric loading. In fact, some of the cases considered are actually unstable. $(d>b)$

Static Stresses in Catenary Arches

As the load line in an arch of uniform weight is approximately a catenary it is clear that the form of arch having a minimum of stresses is a catenary. Table III has been prepared for a series of catenary arches similar to Table I for circular arches.

TABLE III

$\frac{s}{h}$	l	w	θ	R	H
1	1.49	1.49	67.4°	1.61	0.62
2	1.16	1.16	47.5	1.43	1.06
4	1.04	1.04	27.5	2.33	2.01
8	1.01	1.01	14.2	4.10	4.00
16	1.00	1.00	7.1	8.08	8.00
32	1.00	1.00	3.5	16.20	16.00

It will be noticed that the average loads, *R* and *H*, as given in Tables I and III are approximately the same. However, the catenary has no eccentric loading and the stress factors given in Table II for the circle would be unity for the catenary in all cases.

Properties of the Catenary

It is rather difficult to find in one reference the various properties of the catenary, and computation of catenary arches has been considered difficult and laborious. However, if a few simple equations are used, any values can readily be obtained from tables.

The catenary is the curve taken by a uniform flexible chain hung between two supports. In the case of an arch the curve is inverted. An inverted catenary is shown in Fig. 2, plotted on the *X* and *Y* axis. The distance between the *X* axis and the apex of the curve is called the modulus (m) and determines the shape of the catenary.

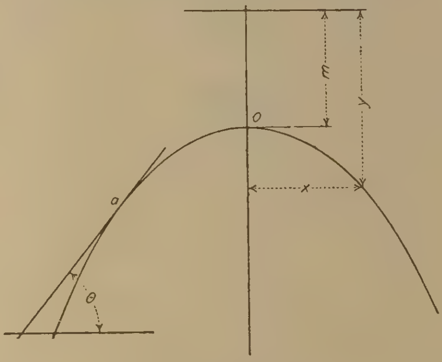

FIG. 2.—Catenary.

The equation of the catenary is:

$$y=\frac{m}{2}\left(\theta^{\frac{x}{m}}+e^{-\frac{x}{m}}\right) \tag{4}$$

or in hyperbolic functions

$$y=m\cos h\frac{x}{m} \tag{5}$$

The latter form is the most convenient to work with.

The slope angle at any point on the curve is given by:

$$\theta = \tan^{-1}\left(\sin h\frac{x}{m}\right) \tag{6}$$

The length of the curve between the apex and any point is:

$$l = m \sin h \frac{x}{m} \tag{7}$$

The radius of curvature at any point is: $r = \dfrac{y^2}{m}$

The compression (or tension) at the apex is:

$$H = wm$$

where w is the weight per unit length of the curve.

It is usually desirable to find a catenary that will pass through three given points, the crown and two skewbacks. That is, we have values of x and $y-m$, and wish to find m.

From equation (5), $(y-m)+m = m \cos h\dfrac{x}{m}$.

It is difficult to solve directly for m in the above equation, so a value for m must be assumed and the equation evaluated. If the two sides are not equal another value must be taken, and so on until a sufficiently precise value is obtained. Much time can be saved by obtaining the initial value of m from the curve in Fig. 3 to suit the ratio of rise to span.

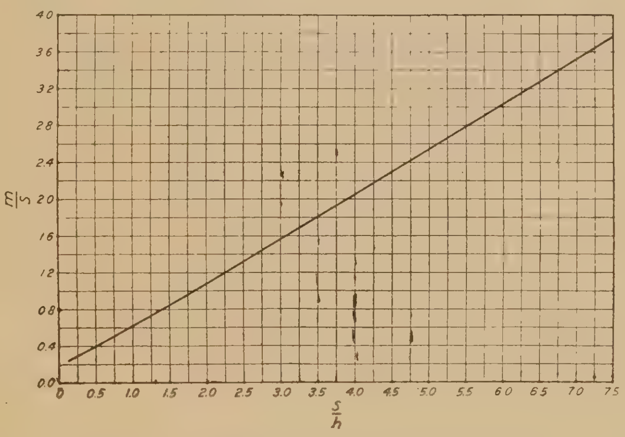

FIG. 3.—Curve for obtaining modulus
Where $s = \frac{1}{2}$ span
h = rise
m = modulus

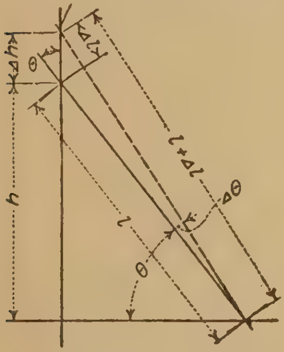

FIG. 4.—Temperature stresses. Change in length.

Temperature Stresses

If a crown is held rigidly between skewbacks and is heated it must rise to a certain extent. This rise causes an increase in curvature at some or all points and therefore pinches the tips of the arch blocks. The exact amount of this rise cannot be calculated because the points of flexure are not determinate. The relative amount for different heights of crown can be calculated as shown in Fig. 4. The increase in height, $\Delta h = \Delta l$ cosec θ, relative values of which are given below.

TABLE IV

$\frac{s}{h}$	θ	cosec θ	Δh
1	45.0°	1.41	0.014
2	26.5	2.24	0.022
4	14.1	4.10	0.041
8	7.1	8.20	0.082
16	3.7	15.6	0.156
32	1.8	35.0	0.35

$s = 1$

The pinching effect is much more severe in flat arches than on high ones.

Another temperature stress is introduced by the unequal expansion of the inside and outside of the crown. This stress is a compression on the hot ends of the bricks.

Both of these temperature stresses tend to compress the hot end of the brick so that when the arch cools the inner ends of the joints are open. This causes instability and uneven stresses that often crack the blocks. The first temperature stress can be reduced greatly, as shown in Table IV by using a high crown. The second type of stress can be reduced by using insulation on the outside to cut down the temperature difference between the inner and outer surface.

Some Applications of the Catenary to Actual Design

For the first example suppose a crown is required for a rectangular kiln with 145 inches between skewbacks. From Table III it is seen that a rise of about 55 inches will give minimum values H and R together.

From Fig. 3 the approximate value of m is found to be 54.

$$(y-m)+m = m \cosh \frac{x}{m}$$

$$55+54 = 54 \cosh^{*} 1.34$$

$$109.0 = 54 \times 2.040$$

$$= 110.2$$

54 is a little too low; next trying 55.0 gives;

$$55.0+55.0 = 55.0 \cosh 1.318$$

$$= 55.0 \times 2.002$$

$$110.0 = 110.0$$

which is sufficiently exact.

It is convenient to tabulate the ordinates and abscissas as shown below. After m has been found it is only necessary to substitute in the various formulas.

---

[*] Smithsonian Mathematical Tables. Natural Hyperbolic Functions.

TABLE V

x	$\frac{x}{m}$	$\sin h\frac{x}{m}$	$\cos h\frac{x}{m}$	y	$y-m$	i	R
0	0	0	1.000	55.0	0	0	55.0
5	.0909	.0910	1.0041	55.2	0.2	5°15′	55.3
10	.1818	.1830	1.0166	55.8	0.8	10°22′	56.6
15	.2727	.276	1.0374	57.0	2.0	15°27′	58.9
20	.3639	.371	1.0670	58.7	3.7	20°21′	62.5
25	.454	.470	1.105	60.8	5.8	25°10′	67.1
30	.546	.574	1.153	63.5	8.5	29°52′	73.2
35	.637	.681	1.210	66.6	11.6	34°17′	80.6
40	.728	.794	1.277	70.2	15.2	38°29′	89.3
45	.818	.912	1.354	74.5	19.5	42°11′	100.8
50	.909	1.039	1.442	79.3	24.3	46°05′	114.2
55	1.000	1.175	1.543	84.9	29.9	49°37′	131.
60	1.091	1.321	1.657	91.1	36.1	52°52′	151.
65	1.182	1.477	1.784	98.2	43.2	55°52′	175.
70	1.272	1.644	1.924	105.8	50.8	58°42′	204.
72.5	1.318	1.734	2.001	110.0	55.0	60°02′	220.

From this table the curve can be laid out full size and the forms made up, allowing ½ the thickness of the arch ring inside the catenary.

The skewback angle is 60°02′.

As the radius of curvature varies between 55 and 220 it might be thought that a large number of special blocks would be needed with different tapers. It will be found, however, that if two tapers are provided, one to fit the short radius and one the long, they can be so alternated as to provide a satisfactory construction. The joints can be 10° or 15° from normal to the forms without harm as the angle at which slip occurs is about 30°.

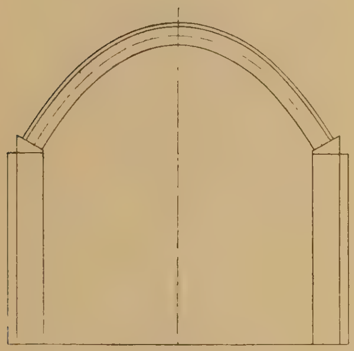
FIG. 5.

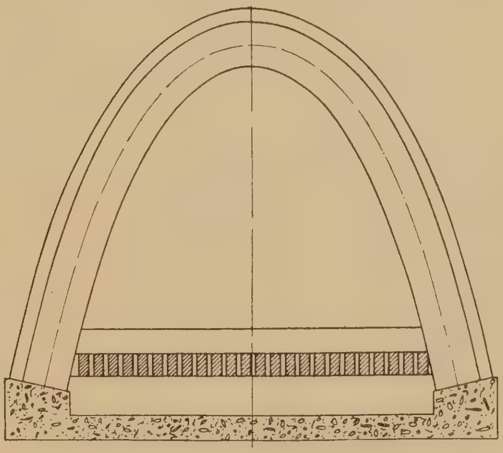
FIG. 6.

This arch is shown to scale in Fig. 5 with a nine-inch ring and 2½ inches of insulation. The load at the skewback is 7.30 lbs. per sq. in. and at the crown 4.03 lbs. per sq. in.

As another example consider a high catenary for a small kiln so as to eliminate the sidewalls. The span will be 84 inches and the rise 69 inches. From Fig. 3, m is 20 and by trial as before more exactly 19.0.

TABLE VI

x	$\frac{x}{m}$	$\cos h\frac{x}{m}$	y	$y-m$
0	0	1.000	19.0	0
5	0.263	1.035	19.7	7
10	0.527	1.142	21.7	2.6
15	0.789	1.328	25.2	6.2
20	1.054	1.609	30.6	11.6
25	1.317	2.000	38.0	19.0
30	1.579	2.528	48.1	29.1
35	1.841	3.231	61.4	42.4
40	2.108	4.177	79.5	60.5
42	2.210	4.613	88.0	69.0

$m=19$

This arch is shown to scale in Fig. 6.

Conclusions

It may be concluded from the above discussion that:

1. High arches have a minimum of static and temperature stresses.
2. High circular arches approach instability and, therefore, are unsatisfactory.
3. High arches of catenary shape are quite satisfactory.
4. Insulation of the crown decreases the temperature stresses.

A number of catenary arches have been tried out on high temperature kilns in direct comparison with circular arches. In every instance they have shown several times the life of the circular arches.

A PRACTICAL GAS-FIRED TEST FURNACE FOR PLANT USE[1]

By H. G. Fisk[2]

ABSTRACT

A gas-fired test furnace of quite general application is described.

Introduction

Many plants have need for a small test furnace for fusion, firing, spalling, slagging and load tests. This article describes a furnace which has proved to be of quite general application, low in construction costs and operating costs, and efficient with either low pressure, natural or artificial gas.

Most furnaces require compressed air not available at many plants. Other furnaces operate by a blower but their use is restricted due to their small size, difficulty in making observations while in operation and in the temperature attainable. The furnace here described overcomes these difficulties.

Construction

The furnace is of the pot type; it is updraft, direct-fired, with two burners arranged tangentially at the bottom. The inside of the furnace is constructed of a ring of arch brick, set on end, forming a circle of approximately twelve inches inside diameter. Resting on the lower ring, a second ring is set in a circle of about nine inches inside diameter. The lower inside edge of the top circle of brick is tapered downward on the inside. (See Fig. 1.) First grade heavy duty fire brick are used for the inside rings which are insulated by outer rings of less refractory brick. Midway and above the points at which the burners enter the furnace, and opposite the blower, is a door of such size that the end of a standard size brick may be inserted on edge. This door is for observation and insertion of trial pieces.

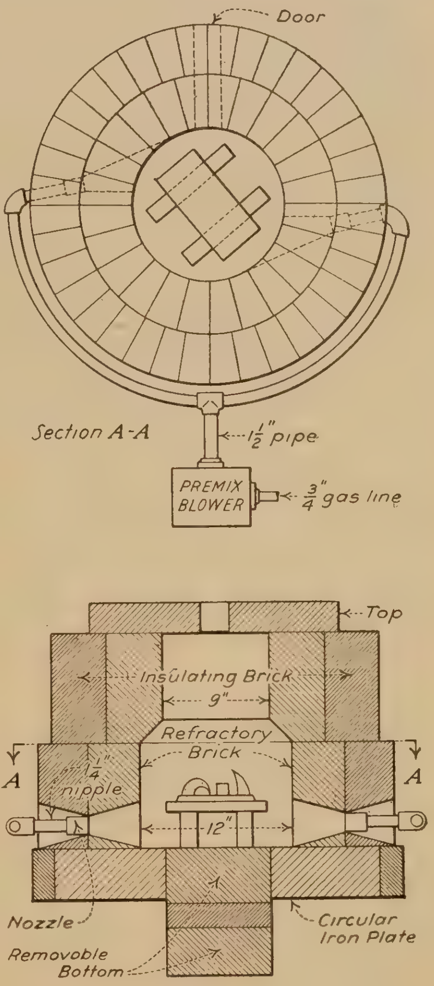

Fig. 1.

The burners enter from opposite sides, and are offset to give a rotary effect to the gases within the chamber. The burner nozzles are flush with the inside of the outer ring of brick and the ports are tapered through the inside ring to allow expansion of combusting gases. The nozzles are sealed with alundum cement. This makes possible operation with greater positive pressure. The mixing blower is set close to the furnace in such a manner as to allow equal distribution to each burner through a one and one-half inch pipe. These pipes are bent to avoid unnecessary sharp turns. The bottom of the furnace is so built as to permit removal to make repairs from the bottom, and to inspect the burner ports from the inside. The direct support of the bottom by bricks from the foundation gives ample rigidity for a load test. The furnace is mounted on a one-half inch thick iron plate with a nine and one-half inch square hole in it to allow the removal of the bottom. The mixing blower, a Maxon Premix Blower No. 5, is operated on 220 or 110 volt alternating or direct current. Iron bands are placed around the outside as shown in Fig. 2 to give strength and rigidity.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division.)

[2] Crescent Brick Company, New Cumberland, W. Va.

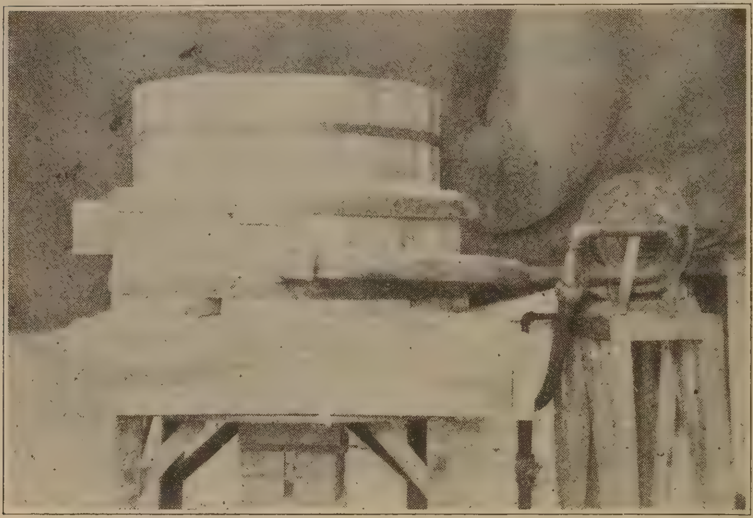

Fig. 2.

Operation

A heating effect equivalent to cone 20 is obtained without any obstruction to the flow of gases in the chamber, but to obtain cone 30 it is necessary to place a checker or box work in the chamber to hold the heat. This checker work can be made to form a muffle protection for test pieces and cone plaques. The best grade of aluminous or flint fireclay brick cut to appropriate sizes has been found to give satisfaction here. In order to constrict the flow of gases from the top of the combustion chamber and to allow a draft adjustment four bricks are set end to side so as to form a hole about 3 inches square over the center of the chamber. These brick permit a variation of draft at will. If desired, two soaps may be placed in the door and observations made by the removal of the top one only. For a spall test the brick to be tested, of standard size, is inserted in the door and withdrawn at intervals for immersions or chillings. The removable bottom permits the tapping of heated or molten charges into water. This permits the preparation of frits and increases the range of usefulness of this installation. Temperature readings may be made through the door with an optical pyrometer, or a thermoelement.

It has been found that at temperatures around cone 30 the checker brick deform due to load and spall due to sudden temperature changes caused by opening the door. The best service at these temperatures has been obtained from cyanite brick.[1] It is thought that temperatures above cone 30 could readily be obtained by the use of carborundum brick for the boxing, as the limiting factor has been the stability of the checker work rather than the temperature of combustion.

Advantages

This furnace has the advantage of allowing rapid heat tests to be made under either oxidizing, neutral or reducing conditions on large or small test pieces. The firing chamber is sufficiently large to accommodate standard size brick. Continuous operation without the necessity of shutting down for the making of observations from the top is possible. It is of rugged construction and will stand considerable abuse. Samples may be withdrawn and introduced through the door without the necessity of allowing the furnace to cool completely, thus making possible a greater number of tests in a given time. There are no expensive parts or shapes to be replaced. The operation on natural gas of pressures as low as two ounces is a decided advantage.

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[1] Cyanite brick, kindly placed at the author's disposal by H. C. Harrison of the U. S. Bureau of Mines.

A CHEMICAL STUDY OF THE ABSORPTION OF SULPHUR DIOXIDE FROM KILN GASES BY CERAMIC WARE[1]

By Frederick G. Jackson[2]

ABSTRACT

Two clays rich in scum-forming bases are studied. One is practically free from sulphur, the other heavily charged with it. Draw trials of these clays are taken from laboratory and commercial kilns at suitable temperature intervals. Commercial firings typify minimum, average and extreme sulphur exposure in coal-fired kilns. Laboratory firings are in imitation of them. The draw trials are analyzed for water-soluble sulphates and bases and the percentages of the appropriate sulphates are presented in the form of tables.

Comparisons of results show that the temperature attained has much more influence on the amount of sulphates formed in the ware than concentration, or time of sulphur exposure. Calculations show that even under the most favorable firing conditions, with 0.5% sulphur coal on a 64-hour schedule of firing, twelve times as much sulphur is available as is actually absorbed. Even under the most severe conditions the concentration of sulphur gases from the coal in the kiln gases is so small, (1%), and the maximum evolution of sulphur gases from the ware is such a small fraction (2.6%) of the volume of kiln gases, that the effect of the former in retarding the formation of the latter according to the Law of Mass Action, must be unnoticeable. It is, therefore, futile to try to avoid sulphate formation with coal as a fuel by seeking a coal low in sulphur. The method of study used is recommended for intensive investigation of firing conditions with the object of attaining maximum economies.

Introduction

The presence of sulphur dioxide in kiln gases has long been known to have a bad effect on ceramic ware. It was early recognized as a cause of scumming by Seger[3] and by Trautwine.[4] Orton[5] has shown the behavior of iron-sulphur compounds present in green ware under various conditions of firing. Previous work by the writer[6] has shown that the sulphur may be present in the ware as any of a variety of compounds. However, the distribution of sulphate between the various bases at different stages of the firing, while hinted at by Orton and Staley, has never been studied quantitatively.

Object of the Investigation

The practical man wants to know how to mature his ware and get it free from sulphur. He wants to do this as quickly and as cheaply as possible. This process resolves itself into several steps. If the fuel contains sulphur, this will be carried into the kiln principally as dioxide. At first this will be oxidized and absorbed by the ware as sulphates if bases are present. At higher temperatures the sulphur gas will (theoretically) resist the decomposition of these sulphates. If the ware contains sulphur in the form of pyrite, this sulphur must be oxidized. One step in its removal is the formation of sulphates. If these sulphates are not subsequently broken down they may cause bloating and black[1] or red[2] cores in the ware. Sulphates remaining in the finished ware will cause scumming and efflorescence.[3]

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[1] Published by permission of the Acting Director, Bureau of Mines, Department of Commerce. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Heavy Clay Products Division.) Received December 31, 1925.

[2] Associate Chemist, Bureau of Mines, Ceramic Station, Columbus, Ohio.

[3] Collected Writings, I, 213.

[4] *Jour. Franklin Inst.*, **105**, 259 (1878).

[5] Orton and Staley, "A Study of the Chemical Status of Carbon, Iron and Sulphur in Clays during the Various Stages of Burning." Third Report of the Committee of Technical Investigation N.B.M.A., 1908.

[6] *Jour. Amer. Ceram. Soc.*, **7** [3], 163; [4], 223; [5], 382; [6], 427; [7], 532; [8], 634; [9], 656 (1924).

This investigation is planned to determine the fundamental processes behind these phenomena. The presence of sulphates in the ware during various periods of the firing is the key to the situation. This investigation is, therefore, a study of the sulphates present in clays during firing. The following questions present themselves; when a clay containing compounds of iron, calcium, magnesium, and the alkalis, is exposed to a sulphurous kiln atmosphere, with which base does the sulphur combine? When pyrite oxidized in such a clay, is there any interchange of bases such as $2FeS_2+MgCO_3+6O_2=Fe_2O_3+MgSO_4+3SO_2+CO_2$? Is there any direct change of bases due to increased temperature, such as $Fe_2(SO_4)_3+3CaCO_3=3CaSO_4+Fe_2O_3+3CO_2$? Can scumming be reduced by changing from a fuel containing much sulphur to one containing only a little? Does the formation of a scum-forming or efflorescing compound require for its formation the intermediate action of some other compound?

The answers to some of these questions may be found by a study of draw-trials from commercial kilns. For comparative results, it is necessary to make tests with the same clay as draw-trials from several different kilns in which the heat treatment is different and with two otherwise similar clays, one containing pyrite and the other practically free from it.

Selection of Material

In selecting clays for such a study, it is important that all of the bases to be studied should be present in sufficient amount to be able to play their proper parts. Two coal-formation clays were selected from the descriptions and analyses of many such given in "Coal Formation Clays of Ohio."[4] One was an Upper Freeport clay from Dennison,

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[1] Orton and Staley, *loc. cit.*

[2] M. C. Booze, "The Effect of Red Hearts in Fireclay Brick." *Jour. Amer. Ceram. Soc.*, **8** [4], 227 (1925).

[3] See F. G. Jackson, "A Descriptive Bibliography of Scumming and Efflorescence," *Bull. Amer. Ceram. Soc.*, **4** [8], 376 (1925).

[4] Geological Survey of Ohio, fourth series, *Bulletin*, **26** (1925).

Ohio, the other a middle Kittanning clay from Zanesville, Ohio. Microscopic examination showed that the Upper Freeport clay contained abundant siderite ($FeCO_3$) but little pyrite. Pyrite (FeS_2) was freely present in the middle Kittanning sample.

ANALYSES

	Upper Freeport	Middle Kittanning		Upper Freeport	Middle Kittanning
SiO_2	57.96	50.05	Na_2O	.51	.14
Al_2O_3	20.78	21.73	K_2O	2.74	3.90
Fe_2O_3	6.18	7.95	S	.05	.87
CaO	.37	.56	Total C	.85	.45
MgO	1.10	1.66	Inorganic C	.51	.14

*As given in "Coal Formation Clays of Ohio"

Commercial Uses

While both of these clays were used commercially, neither one was used without admixture. The Upper Freeport clay was mixed with an equal quantity of shale for making sewer pipe, the Middle Kittanning clay was added to nine parts of shale in making common and paving brick. It was extremely plastic and was introduced to increase the plasticity of the mixture.

Method of Procedure

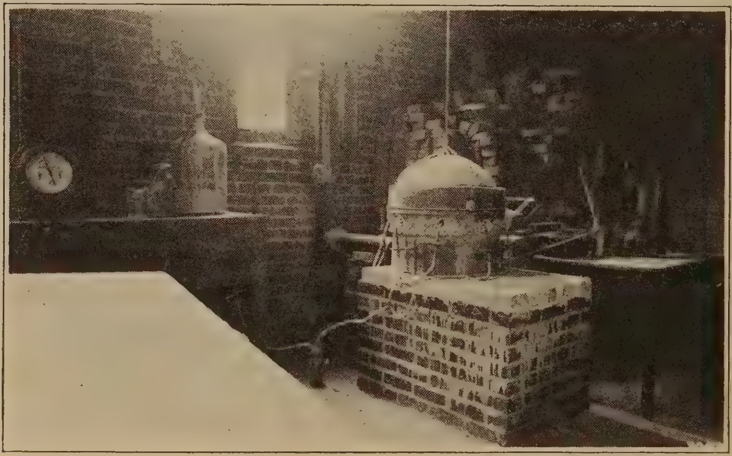
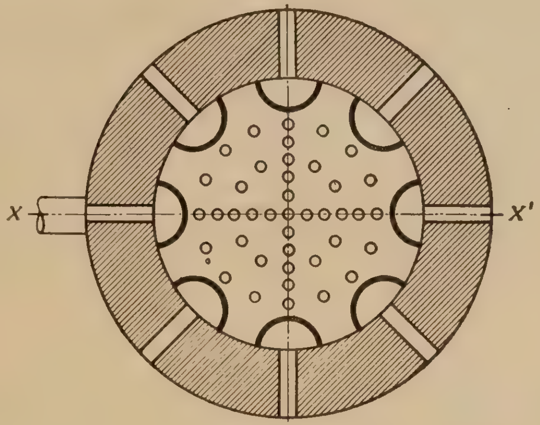


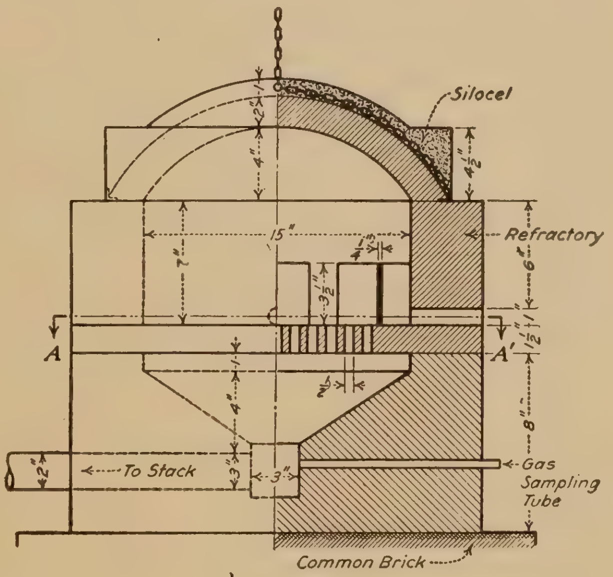
FIG. 1.—Miniature kiln.

Several hundred pounds of each variety of clay were made up into test bricks of special size, ($2\frac{1}{2}$x$2\frac{1}{2}$x7 inches). Several series of tests were made on these in a miniature round downdraft kiln in the laboratory. This kiln was an exact reproduction of a normal 30 ft. kiln with all dimensions reduced from feet to inches and the diameter then halved again making a kiln 15 inches in diameter. The kiln (Figs. 1 and 2) was fired with natural gas from eight bunsen burners which were fed through a manifold. The gas consumption was measured to thousandths of a cubic foot. A device installed between meter and manifold permitted the introduction into the fuel gas of controlled amounts of sulphur dioxide. By this means the sulphur content of commercial kiln atmospheres could be imitated. In the following tests, reproductions were made of kiln atmospheres where coal containing 1%, 4% and 5% of sulphur were imitated. Also, a series on the pyritic clay with a sulphur free atmosphere. Each test represents a separate firing.

In calculating the amounts of SO_2 to be introduced into the gas for these tests, the concentration of SO_2 in the kiln atmosphere was made to correspond to that in a coal-fired kiln. With natural gas as a fuel however, the proportion of hydrogen is so great that considerably less bulk of atmosphere need be passed through the kiln per square foot of kiln floor to effect a definite rise of temperature than with coal as fuel. For comparative purposes it is thus the effect of concentration rather than the amount of SO_2 that is studied.



Section A-A'



Section X-X'

FIG. 2.—Miniature kiln.

Method of Sampling

After each firing, a test brick from the center of the kiln next to the thermocouple was removed. A rectangle 2 inches x 1 inch was marked off on one face. Inside this the material was dug out with a cold chisel to an even depth until about 9 grams has been obtained. This was ground fine in a porcelain mortar and put on a balance pan. About two grams more of material were then removed from the bottom of the hole, ground, and added to the first lot until exactly 10 grams were obtained. In this way all samples were practically uniform in regard to amount of exposed surface included and depth of sampling.

Method of Analysis

These ten-gram samples were then boiled for 30 minutes with 500 cc. of distilled water. They were cooled and allowed to settle over night. Then the water extract was filtered off and refiltered until clear. The clear extracts were each divided into two equal portions, one portion was analyzed for sulphur, the other for acidity, iron and aluminum, calcium and magnesium.[1]

Results

The results of these analyses can best be presented in tabular form. In Table I is given the elapsed time, the temperature, (°F will be used throughout) and the number of grams of sulphur that had entered the kiln per 2 square inches of kiln floor. This unit was selected so that results from kilns of different sizes could be compared and the actual amount of SO_2 impinging upon the amount of surface taken for analysis could be seen. The actual percentages of the different sulphates formed as calculated from the oxides found are then given.

Iron and alumina were determined together and calculated as ferric sulphate. This was done for simplicity. It seemed unnecessary to distinguish between the two. The SO_3 required to form these sulphates is subtracted from the total SO_3 and the remaining SO_3 is calculated to K_2SO_4 because it seemed probable, on account of the large amount of potash present, that potash was the base with which this SO_3 was combined.

These figures point toward some rather surprising conclusions. Confirmatory tests were therefore made in commercial kilns and the results of these will be presented before any discussion is taken up.

Commercial Kiln Tests

Tests were made in three different commercial kilns. In these the sulphur contents of the coals used, the nature of the kiln charges, and the duration of firing were greatly divergent. The first kiln was fired with 32,000 pounds of coal containing 0.5% volatile sulphur. It was 30 feet in diameter, had 8 dead-bottom fire boxes and was charged with 108,000 pounds of drain tile. A temperature of 1790°F was attained in 64 hours.

The second kiln was fired with 25,600 pounds of coal containing 1.0% volatile sulphur. It was 32 feet in diameter, had 9 dead-bottom fire boxes and was charged with 87,000 pounds of sewer pipe, mostly 12 inch. A temperature of 1855°F was attained in 90 hours. The Upper Freeport clay was alone tested in this kiln.

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[1] In these dilutions, the limit of solubility of calcium sulphate, 1 gm. in 500 cc. was not approached. Although but slightly soluble, it forms scum and efflorescence like the more soluble salts and is properly classified among them.

The third kiln was fired with 95,680 pounds of coal containing 5.0% volatile sulphur. It was 30 feet in diameter, had eight inclined grate fire boxes and was charged with 23,400 common brick and 20,640 paving brick, total weight 325,040 pounds. Firing was kept up for 10 days, but 1840°F was reached in 177 hours with 64,850 pounds of coal. The test was stopped at this point.

TABLE I

TESTS IN MINIATURE KILN

Upper Freeport Clay

Draw trial no.	Time fired hrs.	Temp. °F	Gms. S 2 sq. in. floor	Fuel equiv. of atm. %S	Per cent $(Al+Fe)_2(SO_4)_3$	Per cent $CaSO_4$	Per cent $MgSO_4$	Per cent $K_2(?)SO_4$	Per cent SO_3
0	0	unfired clay	0	0	.035	.010	.042	.141	.138
1	5	925	.067	¼	.070	.267	.144	.311	.478
2	5	925	.150	½	.080	.214	.150	.371	.492
3	5½	925	.201	¾	.095	.238	.174	.342	.514
4	4	770	.170	1	.055	.231	.066	.462	.452
5	5½	925	.277	1	.020	.371	.195	.583	.688
6	7	1075	.674	1	.070	.287	.126	.155	.386
7	3¾	795	.730	4	.070	.126	.057	.439	.412
8	5	925	.913	4	.075	.355	.150	.578	.694
9	5½	1075	1.30	4	.100	.529	.240	.284	.698
10	3¾	770	.99	5	.015	.146	.114	.644	.550
11	4	840	1.26	5	.075	.194	.078	.648	.542
12	6	925	1.71	5	.112	.389	.216	.473	.720
13	5	1075	1.88	5	.045	.199	.120	.272	.394

Method of Procedure

The method of procedure with each kiln was identical with minor exceptions. In the setting of the kiln, a little space was left before the wicket. Here, on a platform about 2 feet above the floor and 7 feet in from the wicket, the test pieces were piled. A base metal thermocouple was installed with its unprotected tip close to the test pieces. At appropriate intervals (generally eight or twelve hours) the temperature was read and a drawing was made of one of each variety of test piece. A close record was kept of the time and amount of coal added at each firing. It was then possible to calculate the amount of sulphur which had passed over the trial before it was drawn. This is shown in the tables of results.

The draw trials were sampled and the samples analyzed in exactly the same way as the trials from the miniature kiln. Results of analyses are given in the following tables. The two coal-formation clays were tested in the first kiln, the Upper Freeport clay alone was tested in the second, while in the third were the two clays and the factory mixture of 90% surface shale, 10% Middle Kittanning clay.

TABLE II
TESTS IN MINIATURE KILN
MIDDLE KITTANNING CLAY

Draw trial no.	Time fired hrs.	Temp. °F	Gms. 2 sq. in. floor	Fuel equiv. of atm. %S	Per cent $(Al+Fe)_2(SO_4)_3$	Per cent $CaSO_4$	Per cent $MgSO_4$	Per cent H_2SO_4	Per cent $K_2(?)SO_4$	Per cent SO_3
0	0	unfired clay	0	0	.015	.233	.042	−.056	0	.118
1	2⅓	755	0	0	0	.481	.114	0	.440	.620
2	4¾	840	0	0	.290	.860	.654	0	.028	1.156
3	5	990	0	0	.105	.753	.762	0	.350	1.200
4	6	1075	0	0	.195	.782	1.350	0	.505	1.770
5	6	1545	0	0	0	.782	.492	0	.338	1.028
6	9	1620	0	0	.150	.646	.276	0	.605	1.010
7	2½	740	.170	1	.130	.379	0	0	.168	.400
8	4⅓	840	.214	1	.150	1.035	.325	0	.673	1.290
9	5½	990	.315	1	.065	.641	.180	0	.411	.778
10	6⅔	1075	.441	1	.210	.884	1.350	0	.071	1.648
11	6	1420	.680	1	.655	.792	.390	0	.382	1.344
12	3⅔	770	.995	5	.020	.714	.348	0	.187	.774
13	4	840	1.26	5	.090	.777	.474	0	.396	1.060
14	6	925	1.71	5	.212	.986	.900	0	.447	1.572
15	5	1075	1.88	5	.110	.753	.672	0	.502	1.252

Discussion of Results

Amounts of Sulphur Dioxide Absorved

The most striking fact brought out by these data is the lack of absorption of increasing amounts of sulphur by the ware with increasing amounts of sulphur in the kiln atmosphere.

In Table I are shown the results of firing six samples of Upper Freeport clay to 925° in the miniature kiln with varying amounts of sulphur exposure. These results are compared with other tests of the same clay in commercial kilns to about the same temperature in Table IX.

In the tests in the miniature kiln, where the times of exposure are short and almost the same (5 to 6 hours) the percentages of sulphur absorbed in the extreme cases of ¼% S and 5% S (fuel equivalent atmospheres) are 0.340 and 0.582 respectively. These figures are in the ratio of 10 to 17. In the extreme case of exposure to 5% S for 81 hours, there is only 3.5 times as much absorbed as with ¼% sulphur in 5 hours. Analysis of the clay shows .37% CaO which would combine with .53% SO_3 and 1.10% MgO which would combine with 2.20% SO_3. There are also 2.74% K_2O and 6.18% Fe_2O_3 which might act. The amount of SO_3 absorbed is therefore not limited by the amount of bases present but is almost entirely a function of temperature alone.

Considering now the case of Table I, test 5, where .277 gms. of sulphur per 2 square inches of kiln floor (1%S) entered the kiln. This amount of sulphur therefore impinged on the surface taken as a sample. If it had all been absorbed in the layer about $\frac{1}{4}$ inch deep which composed the sample, there would have been .6925 gms. of SO_3 formed. In the 10 gm. sample this would have been 6.925% SO_3. Analysis showed .688% SO_3 present. Therefore .550% SO_3 was absorbed: less than 8% of the possible amount of absorption. The proportion is almost the same in Table III, test 5, a commercial kiln test with the same concentration of sulphur. In the minimum case of $\frac{1}{4}$% S for 5 hours there was enough sulphur passing to have made 1.675% SO_3. 0.340% was taken up, or only 20%.

At the other extreme, in Table VI, test 6, 2.72 gms. of sulphur impinged on the area removed for sampling, equivalent to 6.80 gms. of SO_3 or 68.0% of the sample analyzed. Absorption was 1.196%. Therefore only 1.76% of the sulphur passing over the clay was retained as sulphate in the sample taken.

It is therefore evident that in any case at these temperatures, only a small proportion of the sulphur in the kiln atmosphere combines with only a small proportion of the available bases.

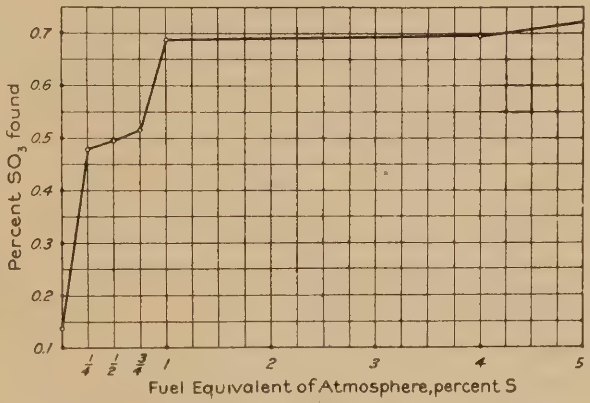

FIG. 3.—The effect of concentration of sulphur on amount of sulphur absorbed. Upper Freeport clay fired in miniature kiln in 5 to 6 hours to 925°.

Figure 3 shows the effect of changing the concentration of the sulphur in the kiln gases. The six tests plotted were all fired in the miniature kiln in 5–6 hours to 925°F with different sulphur contents of the kiln atmosphere. The percentage of SO_3 found on subsequent analysis in each case is plotted against the percentage of sulphur in a coal that would give a similar atmosphere to the one used.

The surprising point is brought out that a large proportion of the maximum absorption is brought about by kiln gas very low in sulphur content. Strange as it may seem, these determinations appear to point to the conclusion that variations in the sulphur content of coal within commercial limits will have little difference in effect on the amount of sulphur combined in the ware.

Let us compare these laboratory experiments with results found from commercial kilns. In such a comparison the element of time enters largely.

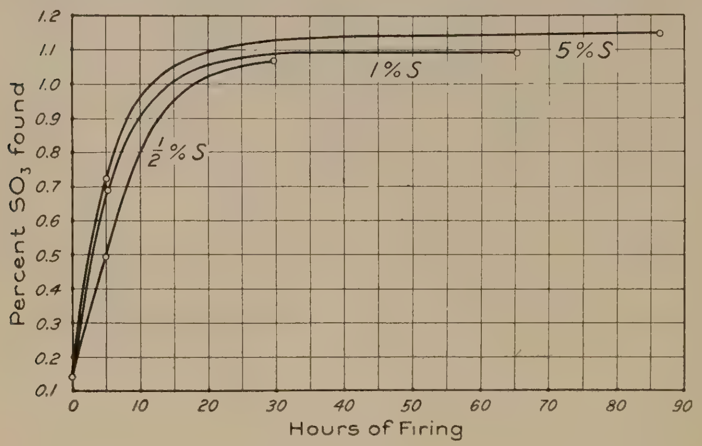

FIG. 4.—The effect of time of expourse to various concentrations of sulphur on the amount of sulphur absorbed.

The effect of time of exposure is shown in Fig. 4. Here the same sort of clay in all cases is fired to 925°F in various kilns. The percentage of SO_3 found is plotted against the time of firing. The curves connect points where the concentration of sulphur in the kiln atmosphere was the same.

The laboratory data are confirmed by these results and an additional point brought out. Variations in the time of firing to 925°, within commercial limits, as well as variations in the sulphur content of the coal, appear to exert little difference in effect on the amount of sulphur absorbed by the ware. This does not seem so impossible when it is realized that, as already shown, the ware exposed to ½% S coal gas for 29 hours was offered by this gas 12½ times as much sulphur as it accepted. With such a tremendous excess of sulphur present in the minimum commercial case, it seems reasonable that little more absorption would be caused by a great increase of this excess. But further evidence from commercial practice in this regard would be most valuable.

Conditions at other temperatures are compared in Table X. At 770°, with rapid heating, the concentration of sulphur has some effect. If the amount of SO_3 in the green clay is subtracted from the amount found in the first two tests cited, it is evident that five times as much sulphur in the gas has increased the amount absorbed in the ware by one third. Under two commercial conditions twice and one-half as much time or six times as much sulphur makes a difference of only 8% between one case and another. When laboratory tests are compared with commercial tests, the time factor is greatly varied. Such time differences at 770° exert a marked effect on the amount of sulphur absorbed.

Thus far we have been studying conditions when sulphur compounds are being absorbed. Above 1000°F the sulphates that have been formed are decomposed. What effect has sulphur in the kiln atmosphere on these decompositions?

The decomposition of a sulphate by heat takes place according to the reaction:

$$MSO_4 = MO + SO_3$$

The Mass Action Law says that a reaction is retarded by the presence of one of its products, but the sulphur in the coal burns in the presence of carbon to SO_2. Inside the kiln, in the presence of glowing hot clay, a fairly good catalyst, there is some tendency for the equilibrium to be set up:

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

It is a good deal of a question, however, whether this would come at all close to equilibrium. When it is realized that the kiln gases from a coal containing 5% volatile sulphur burned with 100% excess air would contain only 1% by volume of SO_2 if all of the sulphur went to this compound, it is evident that there is only a small fraction of a per cent of SO_3 at the most in the gas.

TABLE III

UPPER FREEPORT CLAY FIRED ON 64-HOUR SCHEDULE WITH COAL CONTAINING 0.5% VOLATILE SULPHUR

Draw trial No.	Time elapsed hrs.	Temp. °F	Gms. S per 2 sq. in. floor	Per cent $(Al+Fe)_2(SO_4)_3$	Per cent $CaSO_4$	Per cent $MgSO_4$	Per cent $K_2(?)SO_4$	Per cent H_2SO_4	Per cent SO_3
0	0	unfired clay	0	.035	.010	.042	.141	0	.138
1	22½	600	.315	.200	.078	.114	.296	0	.406
2	26	735	.390	.045	.325	.160	1.000	0	.902
3	27	775	.416	0	.306	.205	1.205	0	1.012
4	28	840	.434	.020	.442	.285	.910	0	.976
5	29	925	.478	.020	.549	.305	.910	0	1.072
6	30	990	.504	.035	.355	.198	.532	0	.665
7	31	1075	.548	.240	.277	.138	.070	0	.460
8	45	1545	.944	.260	.083	.141	0	−.178*	.154
9	52	1760	1.17	.105	.063	.126	0	−.086	.114
10	64	1790	1.49	.090	.044	.111	0	−.130	.048

* Negative amounts of sulphuric acid found by difference, are due either to slight experimental inaccuracies or to the formation of soluble salts of the bases other than sulphates.

Let us now assume that the bricks in the third commercial kiln tested (5% S coal) had all been made of Upper Freeport clay. This clay has very great absorptive power for sulphur. The weight of charge was 325,040 pounds. This clay showed its greatest decomposition of sulphates between 105 hours and 117 hours in this firing. 0.712% SO_3 was evolved. If the entire kiln charge had lost at this rate, there would have been 2317 pounds SO_3 evolved, equivalent to 927 pounds of sulphur, during the twelve hours. During this interval 7100 pounds of coal were fired which contained 355 pounds sulphur. This sulphur, burning to SO_2, formed only 1% of the kiln atmosphere. Therefore the 927 pounds S evolved from the ware would form only 2.61% of the kiln atmosphere.

TABLE IV

MIDDLE KITTANNING CLAY FIRED ON 64-HOUR SCHEDULE WITH COAL CONTAINING 0.5% VOLATILE SULPHUR

Draw trial no.	Time elapsed hrs.	Temp. °F	Gms. S per 2 sq. in. floor	Per cent $(Al+Fe)_2(SO_4)_3$	Per cent $CaSO_4$	Per cent $MgSO_4$	Per cent $K_2(?)SO_4$	Per cent H_2SO_4	Per cent SO_3
0	0	unfired clay		.015	.233	.042	0	−.056*	.118
1	22½	600	.315	.075	.288	.111	0	−.075	.228
2	26	735	.390	.525	.665	.588	.078	0	1.144
3	27	775	.416	.005	.282	.114	.097	0	.312
4	28	840	.434	0.000	.627	.396	.185	0	.742
5	29	925	.478	.830	.806	.792	.292	.098**	1.752
6	30	990	.504	.660	.844	1.074	−.061	.196**	1.732
7	31	1075	.548	.440	.933	1.134	−.121	.138**	1.610
8	45	1545	.944	.040	.547	.252	0	−.035*	.486
9	52	1760	1.170	.270	.277	.117	0	−.340*	.216

* See foot note to Table III.

** Positive amounts of sulphuric acid are found by actual titration. Slight deficiencies of SO_2 are calculated to K_2SO_4 in these cases for simplicity of expression.

While the small fraction of a per cent of SO_3 from the coal would undoubtedly retard the formation of this 2.61% SO_3 addition to the kiln atmosphere, according to the Law of Mass Action, it is very doubtful if the amount of this retardation could be noticed. Probably the strength of the odor has always deceived the kiln burner as to the concentration of the sulphur gases being evolved.

Selective Action of Sulphur Dioxide

The effect of time and concentration of sulphur dioxide on the selection of bases to form sulphates is an interesting study. The data for this study are assembled in Figs. 5, 6, and 7. In these figures the percentage of sulphate is plotted vertically against temperature. The elapsed firing time is noted below.

There is much of interest in these figures. Ferric sulphate was formed late and persisted long in the 64 hours firing (Table III) while it was reduced below 0.5% by the time 1250° was reached in the two slower commercial firings. Calcium sulphate reached a maximum in all three firings between 750° and 950°. It then begins to decrease and is practically eliminated before 1600° is reached. This apparently is due to occasional short reducing periods caused by intermittent firing.[12]

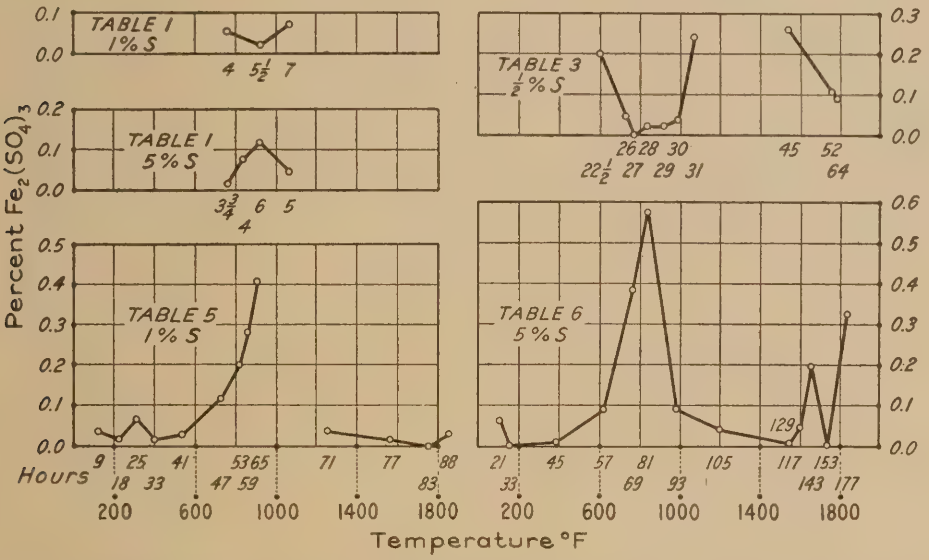

FIG. 5.—The effect of time and concentration of sulphur on the formation and decomposition of ferric sulphate with changing temperature.

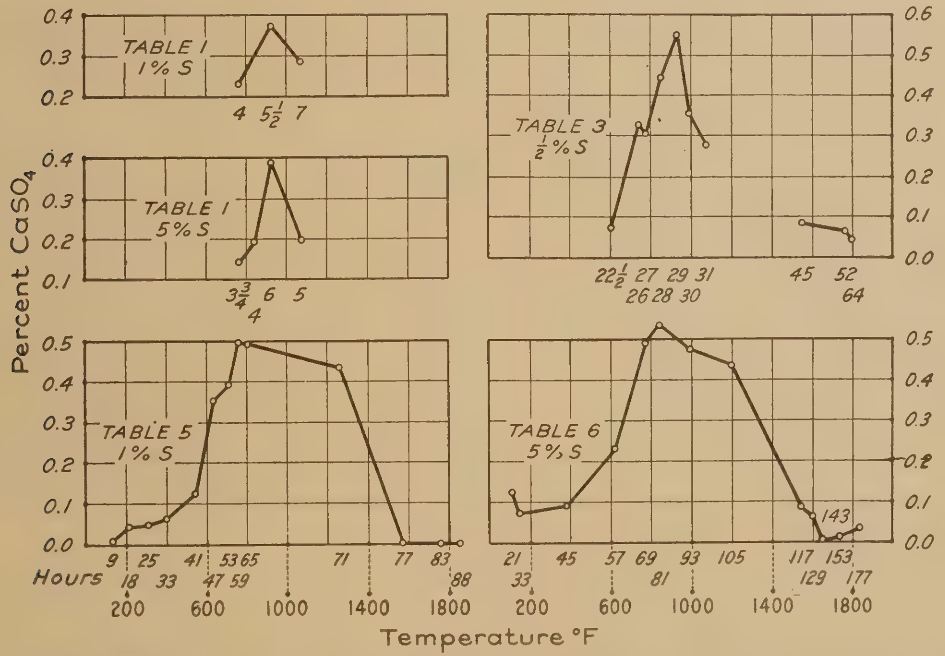

FIG. 6.—The effect of time and concentration of sulphur on the formation and decomposition of calcium sulphate with changing temperature.

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[12] This decomposition by reduction has already been discussed in *Jour. Amer. Ceram. Soc.*, 7 [6], 427 (1924).

In spite of the 1.10% MgO in the green clay, only small fractions of a per cent of magnesium sulphate are formed except in the last case when the sulphur treatment was most severe. This seems to be due to the varied occurrence of the magnesium. Some of it is present as dolomite, easily attacked by sulphuric acid. The rest is combined as silicates which are either insoluble or decompose only slowly under prolonged attack of acids.

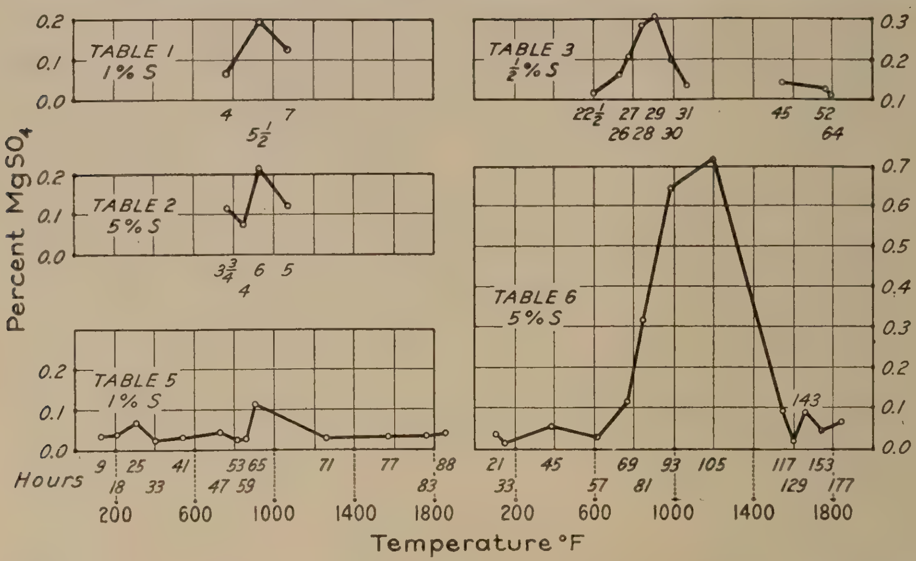

FIG. 7.—The effect of time and concentration of sulphur on the formation and decomposition of magnesium sulphate with changing temperature.

Middle Kittanning Clay

This clay presents a very different problem from the Upper Freeport. Heavily charged with pyrite, (0.87% S), it contains also 0.56% CaO and 1.66% MgO. These are all elements of trouble.

Decomposition of Pyrite

As has already been shown,[1] the decomposition of pyrite depends very greatly on the rate of gas flow over the ware. Quantitative comparisons between different kiln firings are therefore of little value. Data should be taken which are beyond the scope of this investigation in order to compare results.

It is interesting to notice in Table IV that the iron sulphate increased greatly from 600° to 735° and then decreased to nothing at 775° and 840°. This is probably due to the oxidation of some of the FeS_2 to sulphate. The heat of formation of this reaction then started the oxidation of the carbon in the clay. This resulted in a reduction of the sulphate to insoluble sulphide.

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[1] *Jour. Amer. Ceram. Soc.*, 8 [8], 534 (1925).

The two actions may be simply expressed as follows:

$$(600°\text{–}735°)\,FeS_2+3O_2=FeSO_4+SO_2$$
$$(735°\text{–}775°)\,FeSO_4+2C=FeS+2CO_2$$

As soon as this carbon was burned out, the sulphide was again oxidized to sulphate. This sulphate then began to decompose to oxide as temperature increased. This phenomenon has already been brought out in studying the sulphur evolution from mixtures of pyrite and carbon with clay.[1] This step was not brought out in the results in Table VII. The above two reactions may have preceded oxidation during the 12 hours between the sample taken at 615° and that at 770°.

TABLE V

UPPER FREEPORT CLAY FIRED ON 90-HOUR SCHEDULE WITH COAL CONTAINING 1% VOLATILE SULPHUR

Draw trial no.	Time elapsed hrs.	Temp. °F	Gms. S 2 sq. in. floor	Per cent $(Al+Fe)_2(SO_4)_3$	Per cent $CaSO_4$	Per cent $MgSO_4$	Per cent $K_2(?)SO_4$	Per cent SO_2
0	0	unfired clay	0	.035	.010	.042	.141	.138
1	9	130	.076	.035	.010	.033	.325	.240
2	18	212	.170	.015	.044	.039	.287	.230
3	25	310	.270	.065	.050	.066	.172	.214
4	33	400	.289	.015	.062	.021	.459	.330
5	41	540	.390	.020	.126	.030	.340	.306
6	47	735	.548	.115	.355	.042	.700	.718
7	53	810	.680	.200	.393	.024	.777	.824
8	59	860	.742	.280	.499	.027	1.035	1.088
9	65	905	.995	.405	.495	.111	.819	1.090
10	71	1260	1.30	.035	.432	.027	.826	.780
11	77	1575	1.56	.020	0	.030	.088	.084
12	83	1760	1.87	.000	0	.033	.109	.086
13	88	1855	2.08	.030	0	.039	–.037	.022

There was no free acid in any of these test pieces.

Calcium and Magnesium Sulphates

It is interesting to notice that this temporary formation of sulphate at 735° in Table IV was not confined to the iron. Calcium and magnesium sulphates were formed in even greater amounts. It is a question, however, whether these were formed in the other test pieces inside the kiln. There may have been free sulphuric acid developed which did not combine with bases inside the kiln before it was again decomposed by heat. During the laboratory treatment of the sample when the clay, containing dolomite, was boiled with water, the reaction

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[1] *Loc. cit.*

$$\left.\begin{matrix}CaCO_3\\MgCO_3\end{matrix}\right\}+2H_2SO_4=\left\{\begin{matrix}CaSO_4\\MgSO_4\end{matrix}\right.+2CO_2+2H_2O$$

would be bound to run to exhaustion of one of the factors. It is difficult to understand how calcium sulphate once formed at 735° could have been again reduced, even by carbon, at 775°.

TABLE VI

UPPER FREEPORT CLAY FIRED ON 200-HOUR SCHEDULE WITH COAL CONTAINING 5% VOLATILE SULPHUR

Draw trial no.	Time elapsed hrs.	Temp. °F.	Gms. S 2 sq. in. floor	Per cent $(Al+Fe)_2(SO_4)_3$	Per cent $CaSO_4$	Per cent $MgSO_4$	Per cent $K_2(?)SO_4$	Per cent H_2SO_4	Per cent SO_3
0	0	unfired clay	0	.035	.010	.042	.141	0	.138
1	21	110	.157	.060	.126	.036	.133	0	.212
2	33	155	.736	0	.073	.012	.376	0	.272
3	45	390	1.57	.010	.092	.054	.422	0	.344
4	57	615	2.01	.090	.231	.027	.539	0	.546
5	69	770	2.42	.385	.491	.111	.847	0	1.092
6	81	840	2.72	.575	.534	.312	.794	0	1.334
7	93	990	3.56	.090	.476	.642	.405	0	1.000
8	105	*	4.52	.040	.437	.714	.199	0	.886
9	117	1545	5.60	.005	.092	.090	.097	0	.174
10	129	*	6.61	.045	.068	.015	.087	0	.128
11	143	1655	7.73	.195	.010	.087	0	−.087	.110
12	153	1740	8.48	0	.015	.042	.049	0	.066
13	165	1740	9.28	.024	.141	.036	0	−.016	.110
14	177	1840	10.15	.324	.039	.063	0	−.263	.066

* The highly sulphurous kiln atmosphere destroyed the thermocouple and prevented a reading of temperature at these times.

Both calcium and magnesium sulphates are formed to a greater extent at the maxima and persist to higher temperatures in this clay than they did in Upper Freeport clay draw trials taken concurrently from commercial kilns.

A comparison of the results in Table IV with those in Table VII is of interest. In one case this clay, with its elements of trouble, was fired on a very rapid schedule with little exposure to sulphur fumes. In the other it was fired on a very slow schedule with as sulphurous a coal as is commonly used. The slow schedule developed the decomposition of pyrite at a lower temperature, so that at 840° the content of soluble sulphur was almost at its maximum while at the same temperature in the rapid firing it was at less than half the maximum. However, when both kilns had reached 990° the soluble sulphur content in draw trials was in the ratio of 10 to 12 and the percentage of calcium sulphate, magnesium sulphate, and free sulphuric acid were in the same ratio. Therefore, seven times as much sulphur exposure had caused only 20% more sulphur absorption.

TABLE VII

MIDDLE KITTANNING CLAY FIRED ON 200-HOUR SCHEDULE WITH COAL CONTAINING 5% VOLATILE SULPHUR

Draw trial no.	Time elapsed hrs.	Temp. °F	Gms. S 2 sq. in. floor	Per cent $(Al+Fe)_2(SO_4)_3$	Per cent $CaSO_4$	Per cent $MgSO_4$	Per cent $K_2(?)SO_4$	Per cent H_2SO_4	Per cent SO_3
0	0	unfired clay	0	.015	.233	.042	0	-.056	.118
1	21	110	.157	.030	.369	.027	0	-.167	.117
2	33	155	.736	.045	.330	.051	0	-.045	.218
3	45	390	1.57	.020	.452	.045	.029	0	.350
4	57	615	2.01	.025	.471	.048	084	0	.444
5	69	770	2.42	.665	.821	.312	.094	.100	.620
6	81	840	2.72	.805	1.020	.750	.211	.334	2.156
7	93	990	3.56	.540	1.025	1.290	.289	.235	2.390
8	105	*	4.52	.635	.913	1.548	.120	0	2.122
9	117	1545	5.60	.207	.733	.804	.036	0	1.148
10	129	*	6.61	.025	.539	.126	.025	0	.452
11	143	1655	7.73	.025	.296	.036	0	-.124**	.122
12	153	1740	8.48	.045	.126	.033	0	-.067	.068
13	165	1740	9.28	.050	.112	.078	0	-.091	.074
14	177	1840	10.15	.030	.019	.039	0	-.065	.002

* See note to Table VI.

** See note to Table III.

In advancing from 990° to 1545°, the fast kiln reduced the sulphur much more in 15 hours than the slow one did in 24. However, on the next stage, from 1545° to 1740°–60° the slow kiln more than regained the difference. A twelve-hour holding at this temperature in the slow kiln seems to have been of no benefit, to the surface of the ware at least. Although finished products were not obtained, it seems probable that properly matured ware could be produced in either kiln.

On the basis of these experiments, answers can be formulated to the questions suggested at the beginning of this paper.

When a clay containing compounds of iron, calcium, magnesium, and alkalis is exposed to a sulphurous kiln atmosphere, the sulphur combines with the different bases depending on the nature of the

TABLE VIII

90% SHALE 10% MIDDLE KITTANNING CLAY FIRED ON 200-HOUR SCHEDULE WITH COAL CONTAINING 5% VOLATILE SULPHUR

Draw trial no.	Time elapsed hrs.	Temp. °F	Gms. S 2 sq. in. floor	Per cent $(Al+Fe)_2(SO_4)_3$	Per cent $CaSO_4$	Per cent $MgSO_4$	Per cent $K_2(?)SO_4$	Per cent H_2SO_4	Per cent SO_2
0	0	unfired clay	0	.075	.180	.087	0	−.116	.114
1	21	110	.157	.050	.311	.018	.012	0	.232
2	33	155	.736	.035	.306	.003	.046	0	.230
3	45	390	1.57	.130	.340	.006	.146	0	.368
4	57	615	2.01	.135	.359	.246	.129	0	.388
5	69	700	2.42	.035	.665	.123	.748	0	.934
6	81	840	2.72	.205	.777	.546	.415	0	1.188
7	93	990	3.56	.155	.806	1.344	.165	0	1.560
8	105		4.52	.135	.738	1.368	.009	0	1.432
9	117	1545	5.60	.015	.685	.321	.092	0	.882
10	129		6.61	.010	.534	.108	0	−.002	.390
11	143	1655	7.73	.025	.476	.036	.022	0	.332
12	153	1740	8.48	.050	.238	.045	0	−.061	.150
13	165	1740	9.28	.045	.121	.033	.082	0	.168
14	177	1840	10.15	.045	.199	.024	0	−.044	.124

TABLE IX

UPPER FREEPORT CLAY FIRED IN VARIOUS KILNS TO APPROXIMATELY 925° F

Table no.	Test no.	Time fired hrs.	Temp. °F	Grams S 2 sq. in. floor	Fuel equiv. atm. per cent S	Per cent SO_3
0	0	0	unfired clay	0	0	.138
1	1	5	925	.067	$\frac{1}{4}$	.478
1	2	5	925	.150	$\frac{1}{2}$	.492
1	3	5	925	.201	$\frac{3}{4}$	.514
1	5	$5\frac{1}{2}$	925	.277	1	.688
1	8	5	925	.913	4	.694
1	12	6	925	1.71	5	.720
3	5	29	925	.478	$\frac{1}{2}$	1.072
3	6	30	990	.504	$\frac{1}{2}$	.665
5	8	59	860	.742	1	1.088
5	9	65	905	.995	1	1.090
6	6	81	840	2.72	5	1.334
6	7	93	990	3.56	5	1.000

compound in which they exist in the clay and on the temperature. Some silicates seem to resist attack. This may eliminate large amounts of iron, calcium, magnesium, and the alkalis from the possibility of absorbing sulphur. Other silicates yield more sulphates the longer they are exposed to sulphur gases and the stronger the gases. Carbonates existing in the free state are easily attacked by sulphur gases. Trioxide with water vapor and not gaseous sulphur dioxide, however, is the attacking agent. The intensity of the attack therefore increases around 800°F, when kaolinite gives off water of constitution. The attack ceases and the sulphates begin to decompose about 1000°F.

When pyrite oxidizes in such a clay there is evidence of a direct interchange of bases when the temperature is in the neighborhood of 1000°F. Iron sulphate seems to decompose a little below calcium sulphate, and this, in an atmosphere occasionally reducing, a little below magnesium sulphate. Under such circumstances a reaction such as:

$$Fe_2(SO_4)_3+3CaCO_3=Fe_2O_3+3CaSO_4+3CO_2$$

can take place. It is also possible for pyrite to begin oxidizing to form various sulphates and then carbonaceous matter in the clay to burn and reduce the iron sulphate to sulphide without appreciably affecting the other sulphates.

TABLE X

UPPER FREEPORT CLAY FIRED IN VARIOUS KILNS TO VARIOUS TEMPERATURES

Table no.	Test no.	Time fired hrs.	Temp. °F	Grams S 2 sq.in. floor	Fuel equiv. atm. per cent	Per cent SO_3
1	1	4	770	.170	1	.452
1	7	3¾	770	.99	5	.550
3	3	27	775	.416	½	1.012
6	5	69	770	2.42	5	1.092
1	3	7	1075	.674	1	.386
1	6	5½	1075	1.30	4	.698
1	10	5	1075	1.88	5	.394
3	7	31	1075	.548	½	.460
6	8	105	1200 est.	4.52	5	.886
3	8	45	1545	.944	½	.154
5	11	77	1575	1.56	1	.084
6	9	117	1545	5.60	5	.174
3	9	52	1760	1.17	½	.114
5	12	83	1760	1.87	1	.086
6	12	153	1740	8.48	5	.066
6	13	165	1740	9.28	5	.110

There is little possibility of reducing scumming by changing from a fuel containing much sulphur to one containing only a little. Comparative tests with a clay rich in bases show that, under excellent firing conditions almost as much sulphate was formed as under heavy sulphur exposure. Even under these excellent conditions there was twelve times as much sulphur furnished per unit area as there was absorbed in the surface layer one quarter inch deep. Aside from proper drying and firing the prevention of scumming lies in the selection of clays free from scum-forming bases, iron, calcium, and magnesium carbonates.

Water vapor is the only intermediate agent needed for the formation of scum or efflorescence from its constituents in a kiln. It is necessary since the action of a gas on a solid is slight. Reduction of the water vapor in the kiln by thorough drying of the ware and a good draft during water-smoking is the surest method of avoiding trouble and saving time and fuel.

Conclusions

The calculations and results of experiments presented in this paper bring out the following facts, some of which are somewhat at variance with present ideas:

1. Even under extreme conditions of exposure to sulphur gases in the kiln atmosphere, only a small proportion of the bases present in the clay that was studied (iron, alumina, lime, magnesia, and potash) were converted to sulphates.

2. The greatest amount of sulphur absorbed by the ware was at about 925°F.

3. When heated to 925°F in various commercial kilns the ware absorbed little more sulphur from the gases of a coal containing 5% than from one containing ½%S.

4. Under the above conditions the ware absorbed little more sulphur when the ware was fired in 87 hours than when it was fired in 29 hours.

5. Calculations showed that when firing with a coal containing ½%S to 925°F in 29 hours, less than 8% of the sulphur gases which passed over a given surface of ware was absorbed. At the opposite extreme when the coal contained 5%S and 925°F was attained in 87 hours a much lower percentage of the sulphur gases was absorbed and the actual amount absorbed was but little more than in the other case.

6. At higher temperatures the decomposition of sulphates was nearly the same function of temperature in all of the commercial kilns studied. The effect of the Mass Law in impeding the decomposition of sulphates was unnoticeable, due to the low concentration of sulphur gases in the kiln under any circumstances.

7. A reason for this was shown by calculations as follows: A 5% volatile sulphur coal on burning in 100% excess air makes only 1% SO_2 in the kiln atmosphere. Only a fraction of this is converted to SO_3 by catalysis. An entire kiln charge of bricks made from this clay at the time when the sulphates are decomposing most rapidly would evolve SO_3 at the rate of only 2.6% of the volume of gases passing through the kiln. Therefore the dilution of the sulphur gases is so great that the effect of the Law of Mass action is unnoticeable.

This work was carried out from the point of view of the heavy clay products manufacturer only. The conclusions may not be applicable to ware carrying a glaze or one in which a glass bond is developed.

The above method of study is recommended to anyone wishing to determine exactly what is happening to the ware in a kiln. Coupled with a well chosen series of experimental firings, it will serve as a guide to show just where and how much the firing schedule can be shortened. This will lead to the greatest possible saving in fuel, labor and overhead and the maximum output from equipment at hand.

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ORIGINAL PAPERS

THE DEFLOCCULATION OF CLAY SLIPS AND RELATED PROPERTIES[1]

BY E. W. SCRIPTURE, JR., AND EDWARD SCHRAMM

ABSTRACT

In an earlier paper[2] the authors have given the particle analysis and other tests of a number of English china clays, one English ball clay and several domestic kaolins. In this paper are presented the following additional data for the same clays: the carbon content as a measure of organic matter; the change in state of dispersion with *p*H for 20% slips as determined by settling tests; the change in viscosity with *p*H as determined with 40% slips; the alkali absorption for 20% and 40% slips. The more plastic clays are characterized by high organic content, high alkali absorption, and dispersion at low *p*H. Casting slips made up with the different china clays and two ball clays in varying proportions show that ball clay causes fluidity and that the plastic china clays produce more viscous slips than the less plastic.

I. Clays and Clay Slips

In an earlier paper[2] the authors have given the results of a particle size analysis of a number of clays and have shown a general relationship between particle size, state of dispersion, and physical properties. The most plastic clays were characterized by fineness of grain and partial dispersion when made up into 5% suspensions with water. Since this work was done we have encountered an English china clay (which we shall call No. 8) possessing an unusual combination of properties as follows:

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[1] Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Atlanta, Ga., Feb., 1926. (White Wares Division). Recd. Dec. 28, 1925.

[2] *Jour. Amer. Ceram. Soc.*, **8**, 243–52 (1925).

Per cent of particles $<1.7\mu = 43.8$
Suspension in water—flocculent
Modulus of rupture dry = 217 lbs. per sq. in.
Per cent drying shrinkage = 2.9
Per cent total shrinkage (cone 11 half over) = 8.8
Per cent absorption = 16.9
Per cent water of plasticity = 32.0

This clay was highly plastic as judged by feel, had a high dry strength and water of plasticity, and yet was of coarser grain than some of the tender clays (Nos. 1 and 2). It was noted that like most of the plastic china clays it possessed a yellow tone in the raw state although it fired very white. It appeared possible that some of the china clays might contain small quantities of organic colloids which would have an important influence on their properties. As a measure of the organic matter we determined the carbon content of the clays, reported in the earlier work, by ignition in a tube furnace and absorption in barium hydroxide. Blank runs were made treating the clays with acid to prove that the CO_2 did not arise from decomposition of carbonate. The results of these analyses follow:

Carbon Content of Clays

									Eng.		N.
Clay No.	1	2	3	4	5	6	7	8	ball	Fla.	Car.
Per cent C	.024	.030	.034	.060	.035	.063	.049	.112	1.40	.135	.084

We note without exception low carbon content in the tender clays and increasing carbon as the clays increase in toughness and plasticity. It would appear that organic matter may play an important rôle in china clays as well as in ball clays although we have of course not shown directly any relation of cause and effect.

We frequently encounter references to the variability of china clays and an instructive experience along this line may be recorded here. With china clay No. 4 we obtained originally a dry strength of 180. On a later shipment we found 118. Redetermination of the particle size distribution and of the carbon content revealed no fundamental change. However, the new lot of clay gave a flocculated suspension with our water, whereas the old was partly dispersed and we were evidently simply on a different part of the curve of properties. To obtain a closer insight of the relationship between the various properties of clays, it was clearly essential to follow the change in properties of clay slips with alkali addition.

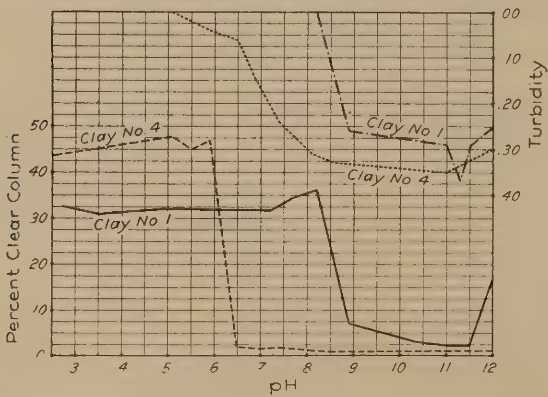

Fig. 1.

Hall[1] describes a method of following the changes of state of clay slips with *p*H of the medium and gives curves for a number of clays. We followed the principle of Hall's method, determining the dispersion by two methods: (1) the rate of settling expressed as percentage of clear column to total height (26 cm.) after 20 hours standing; (2) the turbidity expressed as the grams of solids in 10 cc. of slip taken from a point one inch below the top of the column after 20 hours standing, using NaOH and H_2SO_4 for controlling *p*H. (It will be obvious that the first method is best adapted to the flocculated zone (low *p*H) and gives most accurately the isoelectric point; while the second method is better in the deflocculated range and gives most accurately the point of maximum deflocculation.) The *p*H values were determined colorimetrically on the filtered slips. From the *p*H of slips made up with .02 *N* NaOH the absorption of alkali by the different clays was found. The results of this work are given below in tables and in the curves (Figs. 1 and 2).

TABLE I

SEDIMENTATION TESTS 20% SLIPS

China Clay No. 1

*p*H	2.7	3.5	4.9	7.2	7.7	8.2	8.9	10.3	11.0	11.3	11.5	12.2
Per cent clear column	32.6	31.0	32.2	31.7	34.7	36.2	6.9	3.1	2.3	2.3	2.3	17.3
Turbidity							0.26	0.28	0.29	0.37	0.29	0.25

China Clay No. 2

*p*H	0.6	1.5	1.7	5.0	7.3	7.5	8.7	11.0	11.3	11.9	12.2	12.3
Per cent clear column	39.3	40.0	40.8	38.8	41.5	44.3	1.5	1.3	1.5	1.5	1.5	9.6
Turbidity							0.07	0.14	0.12	0.07	0.06	0.05

China Clay No. 3.

*p*H	2.2	2.7	5.0	5.6	6.25	6.35	6.5	7.1	7.5	8.1	8.4	9.5
Per cent clear column	42.0	41.6	35.1	36.1	36.0	38.2	40.5	37.6	39.8	38.6	7.7	2.3
Turbidity											0.01	0.16

China Clay No. 4.

*p*H	2.5	4.1	5.1	5.5	5.9	6.5	6.9	7.4	8.1	8.6	11.0	12.1
Per cent clear column	43.7	46.2	47.8	45.0	46.8	1.9	1.5	1.9	1.2	0.8	1.0	1.0
Turbidity				0.02	0.04	0.06	0.15	0.24	0.31	0.33	0.35	0.30

China Clay No. 5

*p*H	1.5	1.7	5.1	5.2	5.3	5.7	6.1	6.5	7.1	10.2	11.0	11.2
Per cent clear column	33.4	32.1	25.9	29.0	23.0	21.2	23.8	1.5	1.0	1.0	1.0	1.0
Turbidity								0.01	0.21	0.27	0.27	0.30

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[1] *Jour. Amer. Ceram. Soc.*, **6**, 989 (1923).

China Clay No. 6

*p*H	1.8	2.2	4.5	5.2	5.6	6.0	6.3	6.8	10.0	11.3	12.2
Per cent clear column	23.0	31.5	37.0	33.0	16.2	15.4	5.4	1.5	0.8	0.8	0.4
Turbidity							0.10	0.32	0.30	0.28	0.29

China Clay No. 7

*p*H	1.7	2.0	7.1	7.2	7.3	7.4	8.7	10.0	10.7
Per cent clear column	31.1	28.5	22.3	28.1	27.3	18.1	2.7	1.0	1.7
Turbidity					0.07	0.41	0.52	0.58	0.47

China Clay No. 8

*p*H	2.9	3.9	4.8	5.0	5.8	6.3	6.7	7.9	8.3	9.0	10.0	11.5
Per cent clear column	21.5	27.3	24.6	17.3	21.9	13.5	3.5	1.2	1.0	1.0	1.0	1.0
Turbidity					0.06	0.07	0.09	0.39	0.39	0.39	0.40	0.34

English Ball Clay

*p*H	3.1	3.7	4.3	4.9	5.0	5.1	6.1	6.3	7.8	8.4	8.9	9.5
Per cent clear column	23.2	24.7	31.8	34.1	36.0	36.0	2.3	0.8	0.8	0.8	0.8	0.8
Turbidity					0.01	0.01	0.02	0.43	0.43	0.50	0.56	0.51

Florida Kaolin

*p*H	3.5	4.1	4.9	5.0	5.2	5.3	5.4	5.6	5.9	6.2	7.2	8.0
Per cent clear column	41.6	42.3	40.2	41.4	39.6	40.6	40.3	39.8	38.9	40.8	2.2	1.5
Turbidity											0.04	0.32

Refined North Carolina Kaolin

*p*H	7.4	7.5	8.2	8.5	8.7	9.1	9.3	9.7	10.3	10.6	11.0	11.1
Per cent clear column	15.3	9.7	16.5	15.7	14.6	5.5	3.6	1.9	1.2	1.5	1.5	1.9
Turbidity								0.03	0.13	0.41	0.49	0.52

In the table below are given *p*H and *p*OH at the isoelectric points of the different clays, *i.e.*, the point preceding the sudden drop in height of clear column:

*p*H and *p*OH at isoelectric point

Clay No.	1	2	3	4	5	6	7	8	Eng. Ball	Fla.	N. Car.
*p*H	8.2	7.5	8.1	5.9	6.1	6.0	7.4	5.8	5.1	6.2	8.7
*p*OH	5.8	6.5	5.9	8.1	7.9	8.0	6.6	8.2	8.9	7.8	5.3

Twenty per cent suspensions were made of all the above clays using neutral water, $pH = 7.0$. The resulting values for *p*H were of similar magnitude to those reported by Hall and were as follows:

Clay No.	1	2	3	4	5	6	7	8	Eng. Ball	Fla. Kaolin	N. Car.
*p*H	5.1	5.5	5.5	4.8	5.1	4.6	5.1	4.6	5.1	4.3	5.0

To illustrate the differences between the various clays in absorbing capacity for alkali, we give below the percentage of the NaOH present absorbed by the clay in a 20% suspension in .02*N*. NaOH.

Clay No.	1	2	3	4	5	6	7	8	Eng. Ball	Fla. Kaolin	N. Car.
Per cent NaOH absorbed	48.8	46.7	40.3	91.1	50.2	74.9	47.2	85.9	96.4	88.9	76.5

In the curve (Fig. 2) we have plotted the following data for the different clays: *p*OH at isoelectric point; per cent carbon content; per cent NaOH absorbed; per cent fine particles ($<1.7\mu$); modulus of rupture dry. Other properties of these clays will be found in the earlier paper by the authors.[1] If we consider the curve and the data in the earlier paper there appears a rather striking relationship between the *p*OH at the isoelectric point, the carbon content of the clay, the absorbing power for NaOH, and the properties such as dry strength, shrinkage, and water of plasticity which are an index of plasticity. We are far from suggesting that all properties of clays can be expressed in terms of any one variable; but it does appear that the position of the isoelectric point which determines whether or not the clay is dispersed in a given sample of water and which in turn is related to the alkali absorption and the organic content of the clay, has an effect of prime importance on the physical properties of the clay, even in the plastic state.

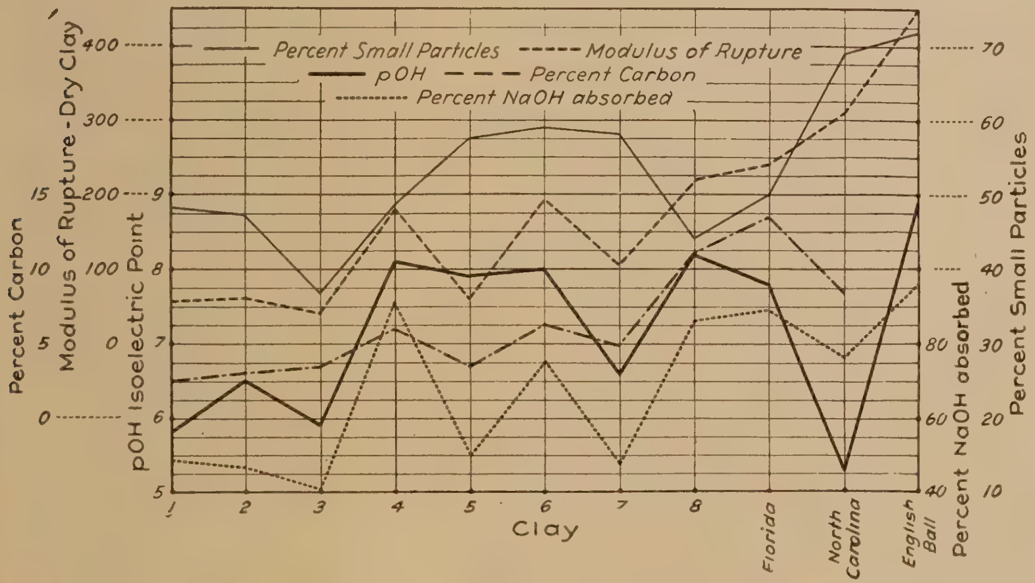

FIG. 2.

To observe the change in state of the clay slips by a physical method which would cover the whole range, it was decided to determine the viscosity-*p*H curves. Viscosities were measured by means of the simple flow type of viscosimeter described by Bleininger.[2] To get a sufficient range of measurements it was necessary to work with slips containing 40% clay. The filtration of these slips in the deflocculated state proved a difficult task. Such slips will filter clear only after a bed of clay has been built up on the filter, but at this point filtration by ordinary means becomes impossible. To overcome the difficulty we constructed a small filter press of brass pipe and flanges, employing a filter of regular press cloth. After the slip was introduced, air pressure was applied and after a short time a clear liquid was obtained. All the slips were made up in a similar manner, allowing the clay to soak over night in distilled water, then blunging with successive small additions of 10 N NaOH. After 20-minute blunging the viscosity was determined and the slip filter pressed for the pH determination. In each case the specific gravity of the slip was 1.32 ± 0.015. We give below the results for the different clays in terms of relative viscosities, OH′ added in mols. per l. of water present, and pH of filtrate. Relative viscosity $= 1.32 \times \frac{\text{time of flow for slip}}{\text{time of flow for water}}$.

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[1] *Loc. cit.* p. 51.

[2] Bur. Stand., *Tech. Paper*, 51.

Table II

Clay No. 1

[OH′]	.0	.0019	.0038	.0063	.0091	.0124	.0166	.0220	.0303
pH	5.2	6.3	6.7	7.3	9.1	10.0	11.1	11.4	12.1
Viscosity	2.82	2.26	2.26	2.20	2.08	1.93	1.83	1.78	1.81

Clay No. 2

[OH′]	.0	.0019	.0038	.0063	.0091	.0124	.0166	.0220
pH		7.5	7.8	7.1	8.5	10.5	11.1	11.7
Viscosity	2.23	2.11	1.97	1.72	1.61	1.57	1.54	1.51

Clay No. 3

[OH′]	.0	.0038	.0105	.0161	.0226	.0310
pH	5.8	6.9	10.1	11.0	11.2	11.7
Viscosity	1.87	1.83	1.76	1.65	1.62	1.60

Clay No. 4

[OH′]	.0	.0019	.0038	.0063	.0091	.0124	.0166	.0220	.0303
pH	4.9	5.2	5.5	5.7	5.9	6.1	6.4	7.0	7.7
Viscosity	2.20	2.02	1.87	1.78	1.72	1.65	1.60	1.54	1.65

Clay No. 5

[OH′]	.0	.0019	.0038	.0063	.0091	.0158
pH	5.1	5.4	6.0	6.9	7.4	9.1
Viscosity	2.34	2.06	1.75	1.62	1.57	1.62

Clay No. 6

[OH′]	.0	.0019	.0038	.0063	.0091	.0124	.0166	.0220	.0303
pH	5.1	5.5	5.7	6.0	6.3	6.7	6.9	7.5	9.1
Viscosity	3.96	3.09	2.52	2.23	2.04	1.69	1.65	1.62	1.62

Clay No. 8

[OH′]	.0	.0019	.0038	.0063	.0091	.0124	.0166
pH	6.3	6.5	6.9	7.1	7.4	7.9	
Viscosity	2.06	2.02	1.78	1.76	1.66	1.69	1.74

English Ball Clay

[OH′]	.0	.0019	.0038	.0063	.0091	.0124	.0166
*p*H		6.1	6.3	6.9	7.0		
Viscosity	2.70	2.78	2.24	1.78	1.57	1.50	1.47

Florida Kaolin

[OH′]	.0	.0038	.0079	.0126	.0154	.0188	.0228	.0285
*p*H	6.9	6.9	7.3	7.5	7.9	8.0	8.3	9.1
Viscosity	No flow	No flow	No flow	4.16	2.38	2.02	1.81	1.74

The relative viscosities are plotted against *p*H in the curve, Fig. 3. These curves are of the same general shape and location as the turbidity and settling curves plotted from the data previously given. Marked differences are observed in the viscosities of the different English china clays without addition of alkali, but at minimum viscosity the differences are slight. The drop in the viscosity curve occurs at a lower *p*H for the more plastic clays but not necessarily at a lower alkali addition because of the higher absorption of these clays. The English ball clay slip reaches a lower minimum viscosity than any of the china clays. Florida kaolin slips are characterized by high viscosity.

In Fig. 4 we have plotted the *p*H against the mols. per liter of OH′ added to the liquid. The broken line is the theoretical curve for the case of no absorption. The departure of the actual curves from this represents the relative absorption of OH′ by the different clays. The results are in agreement with the data previously given for 20% slips and show a greater absorption by the more plastic clays.

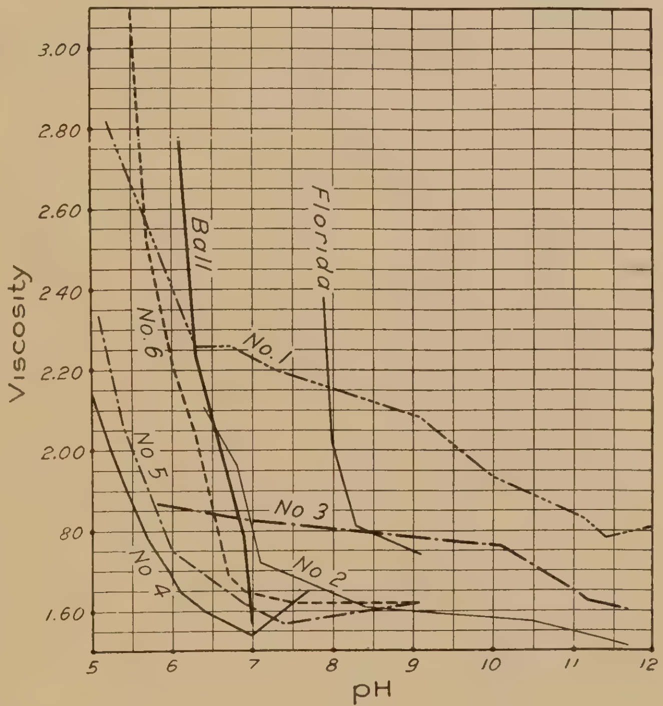

FIG. 3.

II. Body Casting Slips

We next turned our attention to the properties of clays affecting their behavior in casting slips. In the symposium on casting[1] there is a discussion of the question, "What measures should be taken for correcting a slip that requires excessive electrolyte?" Sharply divergent views were expressed as to the behavior of ball clays in casting slips, whether a high content of such clays aided or impeded the production of a low viscosity slip. It could only be supposed that different ball clays might behave in an opposite sense, or perhaps that the same ball clay might exhibit differing behavior under different conditions. Information on this point may be found in the papers by Gerber and by Foltz.[1] To throw further light on the question of the action of different kinds of clay in casting slip we decided to study the behavior of the several clays when used under approximately working conditions. For this purpose mixes were made up containing 50% clay, 30% flint, 20% feldspar. To these were added water to produce a slip containing 67% solids (sp. gr. 1.72), and sodium carbonate below the amount needed for complete deflocculation. The mixtures were run overnight in a ball mill with a few pebbles. The slips so prepared were allowed to stand 24 hours and the viscosities determined after successive additions of concentrated Na_2CO_3 solution. Besides running the individual slips in this way, mixtures were made of china clay and ball

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[1] *Jour. Amer. Ceram. Soc.*, 8, 567–70 (1925).

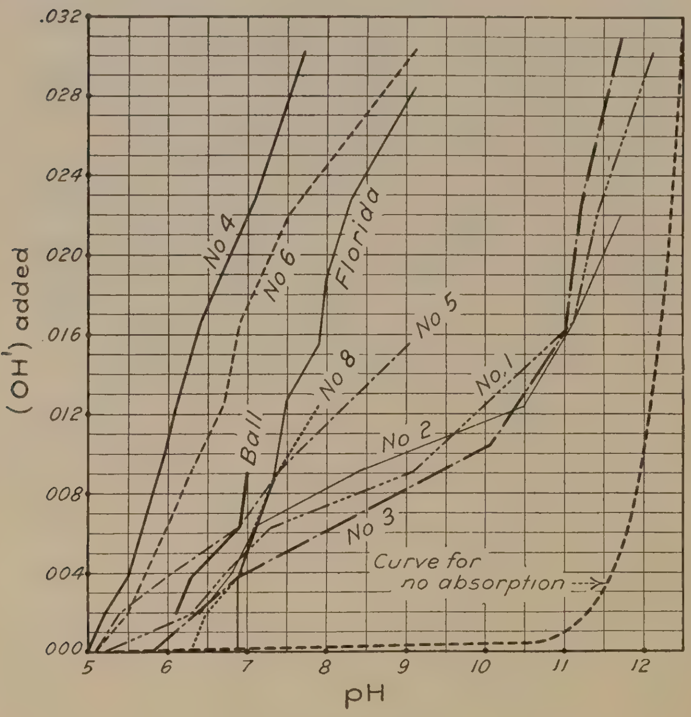

FIG. 4.

TABLE III

Minimum Viscosity

Per cent dark ball clay Per cent china clay	0 50	5 45	12.5 37.5	25 25	37.5 12.5	50 0
China Clay						
No. 1	12.75	4.71	3.32	——	——	——
No. 2	10.10	5.34	3.80	3.41	2.86	3.20
No. 3	8.72	4.41	3.44	——	——	——
No. 4	No flow	No flow	17.8	8.50	——	——
No. 5	14.1	7.75	4.71	4.32	——	——
No. 6	No flow	19.7	6.36	4.56	3.05	3.29
No. 8	No flow	No flow	No flow	7.9	——	——

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[1] *Jour. Amer. Ceram. Soc.*, **8**, 18 and 383 (1925).

Per cent Na_2CO_3 for Minimum Viscosity

Per cent dark ball clay	0	5	12.5	25	37.5	50
Per cent china clay	50	45	37.5	25	12.5	0
China Clay						
No. 1	0.27	0.23	0.27	——	——	——
No. 2	0.29	0.33	0.29	0.29	0.26	0.33
No. 3	0.25	0.25	0.23	——	——	——
No. 4	——	——	——	0.17	——	——
No. 5	——	——	0.15	0.17	——	——
No. 6	——	0.15	0.19	0.27	0.33	——
No. 8	——	——	——	0.33	——	——

Mixtures of Blue Ball Clay and China Clay No. 2

Per cent blue ball	0	5	12.5	25	37.5	50
Per cent china clay No.2	50	45	37.5	25	12.5	0
Minimum Viscosity	10.1	6.64	5.49	4.23	3.83	3.80
Per cent Na_2CO_3	0.29	0.33	0.25	0.29	0.33	0.37

clay slips in varying proportions. A number of different china clays were run with a dark English ball clay and one china clay with a blue ball clay to afford a comparison of these two types of ball clay. The results are given in the preceding tables, the numbers representing relative viscosity and Na_2CO_3 added in per cent of solids present.

Blue ball clay was also tried in combination with No. 4 china clay (25% of each) but it was not possible to produce a slip which would flow. A mixture containing 25% dark ball clay and 25% Florida kaolin also failed to flow.

The data for china clay No. 2 in combination with ball clay are plotted in Fig. 5. We are now in a position to return to the original question as to the effect of increasing or decreasing the ball clay content of a casting slip. From an examination of the curves and tables it is apparent that the important question is not how much alkali need be added to produce minimum viscosity, but how low a minimum can be reached with the different combinations. With all china clay, no low viscosity slip can be prepared. The introduction of a small amount of ball clay results in a sharp lowering of minimum viscosity which continues to fall more gradually with further increase in ball clay content. With dark ball clay the lowest viscosity is reached

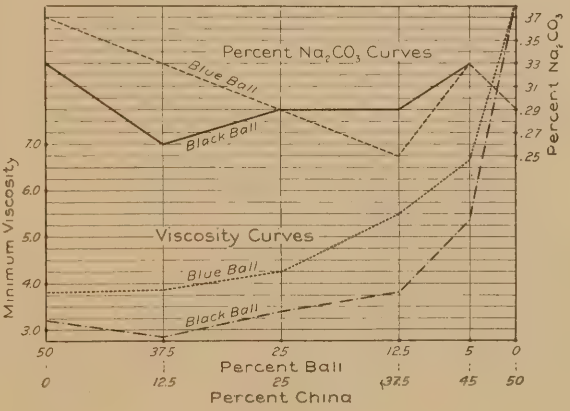

FIG. 5.

in the slip containing 37.5% ball to 12.5% china clay, although the slip with all ball clay gives a figure only slightly above this low value. In the case of the blue ball the minimum is reached with the all ball clay slip.

It is therefore apparent that within the range of practical working compositions an increase in ball clay will give increased fluidity to casting slips. How much ball clay need be used for this purpose depends on the nature of the china clays. The more tender or non-plastic the china clay, the smaller the proportion of ball clay needed to produce a fluid slip. Thus, with china clays 1 to 3 we obtain low viscosity with only 5% of ball clay, with No. 5 we reach a similar condition with 12.5% ball clay, with clay No. 6 we must go to 25% ball clay, while with Nos. 4 and 8 no fluid slips were obtained even with equal quantities of ball and china clays. We thus have the apparent paradox that while the highly plastic ball clays confer fluidity on a casting slip, the more plastic of the china clays have the directly opposite effect.

Considering the behavior of the dark and blue ball clays, it appears that the former gives more fluid slips under like conditions, although the differences are not so pronounced as between different china clays.

As previously remarked, the differences in amount of alkali required do not appear significant and do not follow any simple law. We know from the work done on the simple clay slips that the ball clay is deflocculated at a low *p*H (on the acid side of the neutral point) but has a high absorption factor while the china clays deflocculate at higher *p*H (on the alkaline side) but have lower absorption factors. We are therefore dealing in both cases with opposing effects and the amount of alkali required for the dispersion of mixtures is the resultant of a complex series of properties.

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THE USE OF OVERGLAZES FOR POLYCHROME TERRA COTTA[1]

By A. Lee Bennett

ABSTRACT

The flexibility and economy of single-fire overglazes as compared with other polychrome methods are emphasized. Insoluble materials are preferable. A base white overglaze formula and its preparation and application are given. These single-fire overglazes have been used commercially with excellent results.

Introduction

At present a gradual increase in the use of color in architecture is taking place. With it has been a very considerable increase in the number of terra cotta jobs which are strictly polychrome treatments. Frequently, for a considerable tonnage, three, four, or even more colors are used on each piece of terra cotta. If the colors are obtained entirely by the application of glazes by spraying, work of this character may be quite expensive to manufacture both from the standpoint of time and labor expended.

Polychrome Methods Previously Used

Painting of Colored Glazes Some savings may at times be effected by painting the glazes on to some of the polychromed areas. However, in the writer's opinion, the painting of glazes cannot be considered as satisfactory as spraying them on to the terra cotta. In the first place the average spray or glaze man in a terra cotta plant cannot be depended upon to do a first-class job of painting. Neither is any other properly trained help usually available. Also, if the glazes are painted on the ware, it is frequently difficult to prevent certain very apparent defects due to their being applied too heavy or too light, such as dryness, pinholing or crawling.

These variations in glaze thickness will also tend to cause variations in color which may be undesirable. In addition, the process of painting glaze is frequently quite laborious and may also not present any considerable saving of time as compared with masking of various areas and spraying the glazes. This is especially true if the colored areas are of any considerable size.

Soluble Salts Another possibility for polychroming terra cotta is the production of some of the desired colors either by spraying or painting solutions of soluble metallic salts on the body glaze of the terra cotta.

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[1] Presented at meeting of Pacific-Northwest Section, American Ceramic Society, Seattle, Washington, January 30, 1926. Received January 9, 1926.

Usually with this method of polychroming, the glaze which produces the principal color of the job is applied over the entire surface of the ware and allowed to dry. Then certain soluble salt solutions of definite concentrations are painted or sprayed on to the desired colored areas. Frequently, of course, when the soluble stains are applied by spraying, portions of the piece must be covered so as to prevent any of the solution from falling outside of the areas which are to be colored. Necessarily, any covering of the ware involves considerable time and labor. Also, in spite of such covering, the solution may run under it and stain the adjoining areas. If the solutions are painted on there will sometimes be a tendency toward considerable variations in color, although this may not be a very serious defect. However, we have found in actual practice that our greatest difficulty with soluble salt solutions was the fact that they frequently loosened the glaze coat on which they were applied so that when dry, the glaze would crack and at times fall off the piece, or else, it frequently crawled during the firing of the ware. At present, except for the polychroming of very small areas, we do not attempt to use soluble salt solutions.

The Use of Overglazes for Polychrome

Description and Properties

One other possible method is the use of overglazes to produce various color effects in a single firing of the terra cotta.[1] This process certainly presents excellent possibilities. An overglaze is substantially a mixture of ceramic chemicals preferably insoluble in the liquid used to render them fluid and containing little or no colloidal "clayey" material, which may be applied over the usual glaze when dry and which will develop a glaze texture and consistency upon firing. That is, it consists largely or entirely of non-plastics which will fuse and vitrify on the surface of the glaze itself. Certain of the ingredients may, of course, be chemicals which are ordinarily plastic but which have been rendered non-plastic by calcination. Naturally, such a material or mixture of materials will under ordinary conditions dry very rapidly since it may require but little water, or possibly some other satisfactory liquid, to render it properly fluid and also because of the fact that it does not tend to retain its water or other liquid content as it would if it contained colloidal materials. When dry an overglaze is powdery and does not cohere and knit together like an ordinary terra cotta glaze, for instance, since no colloidal or "setting" action takes place as it drys. Of course, no gum tragacanth, gum arabic or their equivalent is used in the overglazes.

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[1] Hewitt Wilson, "Overglaze Colors at Cones 6–7," *Trans. Amer. Ceram. Soc.*, **19**, 653 (1917).

These, then, are several of the most important properties of true overglazes. As you can see, a true overglaze is a very workable medium for the application of colors. It can be sprayed in an even coating on the surfaces of the ware which are to be polychromed or we have found that frequently it may be painted on with considerable success. Once applied it adheres sufficiently to the terra cotta glaze beneath it so that it will never fall off, nor be at all easily blown off, when dry. It can, of course, be brushed off, this being one of the most important of its properties. Wherever any overglaze is in contact with areas of the ware which are not to be colored by it, it can be so completely removed by brushing with a rather stiff bristled camel's hair or similar brush that the surfaces of the body glaze will come through the kilns clean and "on color." Also since the overglaze does not tend to knit tightly to the dry surface of the terra cotta glaze, this brushing can be done fairly easily and rapidly if only a fair degree of care is exercised.

Colors Developed At the present time we have developed at cone 6 numerous overglaze colors running from white through strong creams to yellows, various shades of brown, blues, greens, blacks, etc., with possibilities, of course, for the development of other colors and the usual limitless combinations of the present palette to give composite shades.

Difficulties One difficulty encountered in the development and use of overglazes is their tendency toward translucency. Also, the fact that their "color reactions" may be influenced by the character of the glaze upon which they are superimposed. Recent tests tend to demonstrate that increasing the concentration of the tin oxide used as an opacifier will eliminate much of the variation in color which may be due to either of these causes.

Another overglaze problem is the fact that some overglazes apparently cannot be resprayed and refired to identically their original color. This seems to be true mainly of those containing fairly large amounts of cobalt oxide or stains containing cobalt.

Suggested Formula We suggest a base white overglaze having the following molecular formula:

$$\left.\begin{array}{l}0.621\ \mathrm{ZnO}\\ 0.379\ \mathrm{CaO}\end{array}\right\}0.453\ \mathrm{Al_2O_3}\left\{\begin{array}{l}1.324\ \mathrm{SiO_2}\\ 0.126\ \mathrm{SnO_2}\end{array}\right.$$

$$\overline{1.000}$$

Various shades of different colors may be obtained by blending the proper stains or coloring oxides with the above overglaze. It is made up entirely from either calcined or non-plastic materials.

Preparation Practically all overglazes are weighed up with about 80% water to the weight of dry overglaze. They are then ground in small pebble mills for three hours. The stains or other coloring ingredients are usually ground separately with the proportions of water and grinding time the same. Then the base overglaze and ground color are screened through at least 100-mesh and blended in the liquid state, in the proper proportions.

Application The mixed overglaze is sprayed on the terra cotta using a very fine spray gun. Our gun is of a suction type and we vary the air pressure between 7 and 10 pounds per square inch depending on the type of overglaze and how it atomizes.

Two even coats are usually applied. A "coat" is applied by spraying over the surface of the piece twice, the second application being at right angles to the first. The overglaze when properly applied is dry and "fuzzy" in appearance and does not cause the dry glaze underneath to blister because of becoming too wet.

Wherever necessary, we cover such adjoining areas of a piece as are not to be colored by the overglaze. The actual covering need not be exact, as the overglaze is easily removed wherever it is in contact with areas other than its own. The method which we have usually employed for the masking of portions of a piece of terra cotta is to cover them with plastic clay (regular terra cotta body) with newspaper separating it from the surface of the piece.

Where only an ornament is to be colored and not the flat backgrounds, pieces of thin sheet iron are cut to the size approximately of the background areas. After spraying, we have found the sheet iron templet to be quickly and easily lifted off with a magnet.

Commercial Use In the actual production of all our recent polychrome jobs, overglazes have been made use of quite extensively.

The jobs have all had from 300 to 500 square feet of strictly polychrome terra cotta, with from two to as many as seven or more colors in addition to the body color of the job on each piece. Most of the colors were produced by overglazes.

Conclusion

I can state definitely that thus far we have found the overglaze method of polychrome both interesting and practical. We certainly hope to satisfactorily develop it further.

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DE-AIRING AS CORRECTIVE IN DRYING[1]

By Fred Brand

ABSTRACT

The physics of mechanical removal of water from clay involves character of pores, adsorption capillarity and it also involves air filled cavities. Theory of clay particle system when plastic is set forth and argument is made for the effect of air on water removal and on drying shrinkage.

Introduction

Seeking for the cause of the phenomenal improvement in drying qualities found in de-aired clays has led to the conclusion that none of the usual theories adequately covered this important phase of ceramic manufacture. We shall not review the various methods used to improve the drying quality of clays but we shall consider some of the theories concerning the fundamental causes for differences in drying behaviors. These theories assume that the drying quality resides within the clay itself which assumption is held not to be altogether according to the facts.

Statement of Current Theory

Perhaps the best general statement of the more current theories is as follows:[2]

In making up dry clay with water to form a plastic mass which may be shaped and molded, the resulting volume is somewhat greater than the sums of clay and water. In this condition the clay particles, both plastic and granular, are surrounded on all sides by a film of water, while small pools or drops fill the cavities and pores between the grains. A tortuous system of capillaries is thus established which are wider in some places and narrower in others. When placed in an atmosphere saturated with moisture, equilibrium conditions are reached when no flow of water whatever takes place in these minute channels. As soon as the humidity is lowered, however, evaporation begins to take place at the surface, and every particle of water thus removed must be replaced through the capillary channels from the interior. The rapidity of this movement depends upon the structure of the clay—*i.e.* whether the capillaries are fine and intricate[2] or coarse and short—and upon the temperature and humidity of the outside air. Open structure, high temperature, and low humidity result in maximum capillary flow and vice versa. Since the spongelike colloidal matter with its immense surface and fine pores offers the greatest resistance to the passage of water, it is obvious that in highly plastic clays the movement of the water through the capillaries must be very slow, it having been estimated that the resistance to this flow is inversely proportional to the fourth power of the diameter of the channels. The capillary flow continues to grow weaker until the films become very thin and finally break altogether. The water remaining within the colloidal interstices and within the pores in isolated films is expelled with increasing difficulty, and, owing to its low vapor pressure, requires a high temperature for its complete expulsion. Clays are subject to two kinds of difficulties which are opposite in character. They may give trouble, due either to an excess of plastic material or to a deficiency of it; in the first case the system of capillaries is so extremely fine that the flow of water through it is very slow and becomes the more restricted as shrinkage progresses. Owing to the fact that such clays show a very large contraction in volume,

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Heavy Clay Products Division). Received Dec. 26, 1925.

[2] A. V. Bleininger, Bur. Stand., Tech. Paper, **1**, No. 1.

the capillary channels become smaller and smaller on drying, thus causing the difficulty of expelling the water to increase. The result is inevitably that the rate of surface evaporation is greater than the flow of water toward the surface, a condition which gives rise to strains and more or less marked ruptures.

In the second case the amount of clay bonding matter is so low that the body does not possess the tensile strength needed to withstand the strain caused by the closing up of the particles near the evaporating surface. The result of this is that the clay gives way and cracks.

In order to overcome these two classes of difficulties some remedial measures are available. These are, for the excessively plastic clays, dilution by means of non-plastic materials like sand or ground, calcined clay (grog), or drying the ware under carefully regulated conditions with special reference to the maintenance of high humidity in the drying until the clay has become uniformly heated throughout, or by using the preliminary heating treatment which is the subject of this work.

In regard to weak clays, lacking in plastic matter, the method for overcoming the difficulty consists in developing the available plasticity to its maximum by means of storing in the wet condition, by grinding and thorough pugging, by the use of slightly acid tempering water (in some cases), and finally by the incorporation of a more plastic material, which offers the most positive solution of the case.

The addition of granular, non-plastic material to an excessively plastic clay is made for the purpose of improving the working quality by reducing its "stickiness," decreasing the drying shrinkage, and with it, the tendency to warp and crack in drying, and of lowering the kiln losses due to strains caused in drying.

If in the case of a difficultly drying, exceedingly plastic clay it is decided to add sand for the purpose of making it easier to dry, this addition should be carried beyond the point of maximum density, so that a larger pore space, and hence an increased evaporation and outlet area, is produced.

The fact that clays generally more or less improve by the treatment indicated makes it appear that the underlying causes of the difficulties and the manner of improvement are as stated by Mr. Bleininger. His explanations, however, do not cover the situation in its entirety. In the case of the feebly plastic clay, why should there be a marked closing up of the surface particles in a clay low in plastic material? Why would not the addition of plastic material also increase this tendency along with the stresses?

Effect of Non-Plastics on Rate of Water Removal

While it is true that in treating a plastic clay with granular material the best results are obtained when the additions are "carried beyond the point of maximum density," yet improvement begins to manifest itself, especially if the clay be worked in the auger machine, long before this point is reached, and throughout the series of additions the plastic material continues to be the fine-pored system through which water must find its way to the surface. Even when the proportion of coarse non-plastic is so large that the fine-pored material is no longer sufficient to fill the voids, giving a so-called "open-pored" mass, there is no freer movement of water to the surface. In fact Bleininger[1] on page 36 says in part as follows:

> In every case it was found that the rate of drying of the preheated clays was identical with that of the normal materials, though, of course, the amount of water required to develop plasticity differed in the preheated materials from the normal amount. In Fig. 7, the curves of clay No. 1 are presented which are typical for all of the materials tested and show clearly that preheating does not influence the rapidity of drying.

Yet in the one we would assume that the capillaries were "coarse and short" and in the other, "fine and intricate" where "the movement of the water through the capillaries must be very slow."

Again, the shrinkage and loss of water curves obtained by Lines[2] show no lag in the rate of drying until two hours after shrinkage had ceased, though of necessity the channels became constantly narrower as drying progressed. Thus if the resistance to the capillary flow is inversely proportional to the fourth power of their diameters, it follows that water diffusion through a clay mass is not due to capillarity in the same sense as water rising in a tube. While loss of weight cannot be proportional to actual replacement to the surface, yet we could reasonably expect a constantly increasing lag as the surface of the water receded from the surface of the mass, if surface replacement was by capillarity.

Drying Time Dependent on Shrinkage

While it is no more difficult to remove water from a sticky plastic clay than from a leaner one, the fact remains that considerably more time is required to safely remove the water from the more plastic clays. Bleininger, to arrive at the approximate time requirements under commercial conditions, multiplies the shrinkage by the time required to remove the shrinkage water under laboratory conditions. Thus in a clay having a shrinkage of 4% and dried in four hours, the answer was 16 hours under commercial conditions, while in a clay shrinking 8.5% in the drying and requiring 8.9 hours the answer was 75.55 hours under commercial conditions.

The Physics of Water Additions

Since the rate of water loss in these two clays is practically the same, why is not the commercial time requirement proportional to the amount of work done?

Regardless of type, clays are made up of varying percentages of various mineral particles, and aggregates of varying degrees of porosity ranging from coarse to submicroscopic. Let us assume that water is added a portion at a time in quantities just sufficient to meet each individual requirement of the mass.

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[1] *Loc. cit.*

[2] E. F. Lines "Notes on the Drying of a Clay," *Trans. Amer. Ceram. Soc.*, **10**, 146 (1908).

Water Absorbed and Adsorbed by Clay Grains

The first portion added would be absorbed by the grains to satisfy their porosity. The next portion added would spread itself evenly over the surfaces of the clay material, and this with the water imbibed by the particles (when the thus wetted particles are brought into contact), forms a system of what may be properly termed capillary water, spreading itself in all directions throughout the mass, and forms the medium through which the attractive forces operate to bring the mass together; an action not unlike that of a water film between two glass plates. Assuming flexible plates roughened by etching or sand-blasting to simulate the irregularity of the clay particles, the parallel becomes more complete. Careful measurement shows the glass plates a little closer together when held by a water film than when dry. The writer, attempting to measure the thickness of this film between superimposed pieces of plate glass, found the pile appreciably shorter when wetted than when measured dry. A similar situation must obtain in the action of the film between the clay particles.

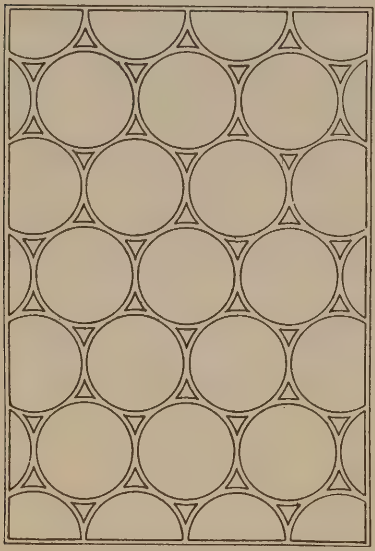

FIG. 1.—Clay mass at its maximum density showing the capillary and filler water systems, the latter shown by the triangles. At this stage there can be no general movement of water to the surface.

The mass at this stage of water content is at its maximum density; any addition or removal of water should cause an increase in volume. This no doubt accounts for the increase in volume which is found in pats of de-aired clays toward the end of the drying period.

Whereas this system is a water carrier it is only more or less efficient as such, for it can act only when the mass is in a rigid condition such as it is at this stage of water content, and when connected to a free moving water supply. Thus on account of the low water content of the mass at this stage of drying, together with the higher temperatures which obtain at this time which would cause capillarity to diminish, coupled with the improbability of any great number of sources of supply, capillarity plays a rather unimportant part in the drying process.

Wetted Clay Particle as a Bubble

It may be of interest to venture for a moment into the more obscure action of this film between the clay particles. We can very properly regard a wetted clay particle as a clay-filled bubble. We know that the tendency of these films is to economize in area. For this reason soap bubbles and drops of water are round, while those of a single plane surface will move loads in their tendency to shrink. They possess energy. This energy in a soap bubble may be shown by directing the open tube to the flame of a candle. The bubble will contract forcing the air out sufficiently to deflect the flame. It is evident that if this bubble or film was within another, the two would give twice the energy. Each enclosing film would add its share of energy toward a common center.

On bringing soap bubbles together into a system of bubbles or suds there is a new alignment of forces, as the system inclines to the spherical, each bubble sacrificing some of its characteristics to the system. Each bubble becoming a segment or member of a larger double walled hollow sphere enclosing smaller spheres of the same character. The whole resulting in a series of concentric or nested bubbles. These nested bubbles are separated by the air contained in the original bubbles but held together by the water films at their points of contact. In this nested form the combined energy of the whole is directed upon a common center. The forcing of this spherical mass into other shapes or forms cannot affect its nested character.

Why Shrinkage is to a Common Center

If a wetted clay particle may be regarded as a clay-filled bubble, it follows that the clay mass at this stage of water content may also be regarded as a bubble mass where the forces strive to align themselves in the same fashion as in the soap bubble system, with this difference—in the soap bubble system the air pockets conform to the film, while in the clay mass the film must adjust itself to the clay particle. Except for the fact that not quite so perfect spheres are formed in the latter, the cases are parallel. In each, we have the same nested system directing their forces upon a common center. In the clay mass with its almost infinite number of these films, together with an enormous number of the contact points, both of which cause forces acting concentrically, we can begin to realize the tremendous energy stored within a wetted clay mass. Regarded in this light we get a rather clear reason why clay shrinkage is toward a common center.

Pore Water

The irregular shape of the clay particles results in many void spaces. The next portion of the water which we would add would just fill these spaces forming a more or less complete system of connected pools of varying shapes and sizes. This system is not a water carrier, in the sense that the water would find egress through it to the surface. The mass still being in a rigid condition, incapable of shrinkage or other readjustment, a general movement of this water would result in a vacuum within the mass. A movement of this water cannot, therefore, take place. Thus this so-called pore system has no part whatever in surface replacement during drying; it is merely a filler.

Water of Mobility

To give the mass flowing qualities as demanded by the plastic processes, a final addition of water is necessary. The introduction of this water, which must be accomplished by force, necessarily causes a wedging apart of the previously wetted clay particles, which in turn results in an increase in volume of the mass. Thus a third system of water, rather layerlike in character, criss-crossing in all directions in uniform area, is produced, crooked slightly, or divided when a clay particle interferes, but maintaining a straight course across intervening pools of filler water. These layers or channels, due to the attractive forces operating within the mass, present their outer terminals to the surfaces in beadlike protuberances, like water above the rim of an overfilled vessel. This is the major water carrying system, in fact the only system in operation during the shrinkage period of drying. Thus the size of the water carrying channels is purely a function of the water of moldability. Their areas or thickness can only vary with the amount of this portion of water added. Thus while they may be "fine" or "coarse" their length depends entirely upon the shape and size of the mass.

It becomes evident too that the wedging apart of the previously wetted clay particles results in the breaking up of the previously formed capillary system. For instead of a continuous system which obtains before the introduction of the final portion of water, the capillary film is now confined to the surfaces of the individual grains. Thus in no case can the capillaries draw from a greater depth than the thickness of the clay particles at the surface of the piece. The breaking up of the capillary system while impairing its efficiency does not altogether destroy it. In a lesser degree only do we have the same attractive forces at work in the same manner and direction as under the discussion of capillary water. The members of the mass at this stage, except as affected by gravity, are in a state approximating perfect suspension, the whole being enclosed and a part of an ideally contractile, concentrically acting system of forces which in the nature of things must promptly respond to any change in equilibrium between the forces operating within the mass and the tension at the surface bringing with them the enclosed and attached clay particles.

The Physics of Water Removal

It thus becomes increasingly evident that water replacement to the surface during drying cannot be due to capillarity, that is, in the sense that the shrinkage water channels act as capillary tubes. Not only do the capillaries or films lack the necessary continuity to the surface, but also because of the fact that so long as the particles which must compose the walls of those tubes are free to contract, the attractive forces will expand themselves not in raising water, but in the bringing together of the walls, thus squeezing the water from between them; an action, which but for the surface tension operating upon the outer terminals of the channels, would force the water of moldability from the mass.

However, as soon as the walls are brought together, which would coincide with total shrinkage, the continuity of the capillary system is again established and capillary movement would again become operative as outlined above and the rate of water loss begins to decrease. Thus in any case, it is not until all danger from cracking has passed, that there is even a possibility of the laws governing capillarity becoming applicable.

We avoid much difficulty in accepting the idea of a squeezing action within the mass, which, instead of giving us enormous resistances which do not show in our experimental drying curves, gives us almost infinite forces to compensate for the constantly narrowing channels during the shrinkage period. We are thus enabled to nicely account for the substantially identical rates of water loss, regardless of the size of the channels.

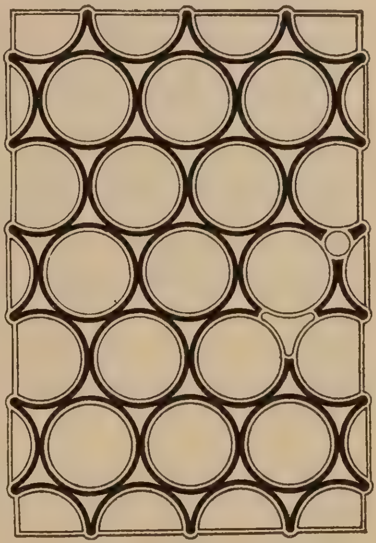

FIG. 2.—Clay mass at the stage of moldability. Capillary films shown by the thin light bands. Filler water by triangles. Water of mobility by heavy lines, while to the right are shown the closing effect of occluded air blebs. Note the capillary films are now confined to the clay particles, except at points where the air blebs make possible their continuity to the surface. In this case only, do they become water carriers during the shrinkage period.

Inasmuch as these forces must diminish as the temperature rises, and vanish when the distinction between the liquid and its vapor ceases, we should expect the rate of water diffusion to be higher at the beginning of drying, than later when the piece becomes heated through. There is just a hint of this in an occasional drying curve, where the drop is a little more rapid during the first hour or so than during the remainder of the shrinkage period. It is to be hoped that someone who is in a position to do so will clear this point by careful experiment.

Air as Cause for Drying Cracks

Since it is while expelling the water of moldability that losses from cracking occur the cause must be in the functioning of the channels. Since there is nothing in a simple mixture of clay and water which would prevent the proper drainage of these channels, we would naturally look for some extraneous cause for the phenomena.

Clays which have been tempered and pugged in contact with air of necessity contain quantities of occluded air. Some of this air will be small blebs which have no effect on the drainage conditions. Most of the air, however, will be in pockets of a larger volume than can be contained in the filler water cavities and encroach upon, or entirely close up the channels formed by the water of moldability, thus effectually shutting off the flow of any water through them. (Fig. 2). These larger blebs regardless of their size can have no effect on the capillary films. Thus while egress to the surface is not entirely cut off by the action of the air bleb, the carrying capacity of the film is not equal to the requirements of evaporation and rupturing strains develop.

The closing up of the major water carrying channels by the blebs is not the only effect produced by them. We must also reckon with the inevitable expansion of this air which takes place under the heat of the drier. Here the blebs are not only expanded in volume with a further choking effect, but the pressures generated often are of sufficient force to cause ruptures even in saturated atmospheres where no drying whatever takes place. This is probably a very frequent cause of breakage among the fine grained, feebly plastic types.

Then again the presence of air within the clay mass has a serious effect upon its strength. It is possible to almost entirely neutralize the effect of plasticity by working air into the mass. Add to this the closing effect of the blebs and the expansion under heat of the drier and we have no difficulty in explaining drier losses.

The more plastic or tighter the clay, the greater the effect of a given quantity of occluded air upon the water carrying channels, and the less the opportunity for the air to escape from the mass. On the other hand, the more open the clay, the less a given quantity of air would affect the drainage system, and the easier would be the escape of the air through a more complete and less resistant pore system.

Hydraulic-Press Brick Co.
Roseville, Ohio

PROPERTIES OF SILICA BRICK FROM COKE OVEN WALLS[1]

By Sandford S. Cole[2]

ABSTRACT

Silica shapes from coke ovens were tested to see what change had occurred after long service. Brick from Chicago and Birmingham districts were examined. Chemical analyses: specific gravity, porosity, fusion values and petrographic examinations were obtained on the samples.

Introduction

Silica brick from the walls of open hearth steel furnaces have been studied by several investigators. V. P. Sokolov[3] in a report upon silica brick used in Martin furnaces claimed the formation of asmanite instead of tridymite. A discussion in an anonymous article[4] gave reasons for the changes occurring in silica brick from an open hearth furnace. C. S. Graham[5] reported analyses made on silica brick from a basic open hearth according to the color zones formed in the brick. An examination was made by M. Meredith[6] and also by J. E. Stead[7] of brick from the roof of an open hearth. H. Thomas, A. Hallen and E. Rodley[8] gave analyses and photomicrographs of silica refractories from a furnace. D. W. Ross[9] examined silica brick from a glass furnace and found tridymite and calcium monosilicate formed on the interior, with the exterior of cristobalite and quartz. The first work, where slag did not come in contact with the silica, was done by A. A. Klein and L. S. Ramsdell[10] upon brick from a tunnel kiln. The quartz was found to be converted to a large extent to tridymite. W. J. Rees'[11] photomicrographs of various sections of a silica block from an open hearth furnace showed the conversions which had occurred. In the work previously reported the formation of tridymite seems to occur on the hot face of the brick. A partial conversion of the cristobalite to tridymite, and a nearly complete conversion of quartz to cristobalite and tridymite occur in the hotter zones.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (White Wares Division.) Recd. Dec. 28, 1925.

[2] Industrial Fellow, Koppers Co. Laboratories, Mellon Institute, Pittsburgh, Pa.

[3] Zapisti Imp. St. Petersburg, *Mineral Obshch.*, **44**, 473 (1908).

[4] *Soc. Chem. Ind.*, **29**, 880 (1910).

[5] *Iron and Coal Trades Rev.*, **102**, 639 (1918).

[6] *Can. Machy.*, **31**, 167 (1919).

[7] *Trans. Ceram. Soc.* (Eng.), **18**, [2] 384–87 (1919).

[8] *Brit. Geol. Survey*, **16**, 115 (1920).

[9] *Jour. Amer. Ceram. Soc.*, **4**, 65–67 (1921).

[10] *Ibid.*, **4**, 805 (1921).

[11] *Ibid.*, **8**, 40 (1925).

Purpose of the Present Investigation

Very little study has been made of silica brick from coke oven walls. In this investigation, the two samples of brick examined came from different manufacturing districts and had been used in two types of furnaces. The purpose of the examination was to determine the general condition of the silica brick after use. The brick had been in service for the same length of time and were located in the same relative positions in the oven walls. However, variations in test results after service might be expected, since the brick were made of different ganisters and had doubtlessly been subjected to different operating conditions.

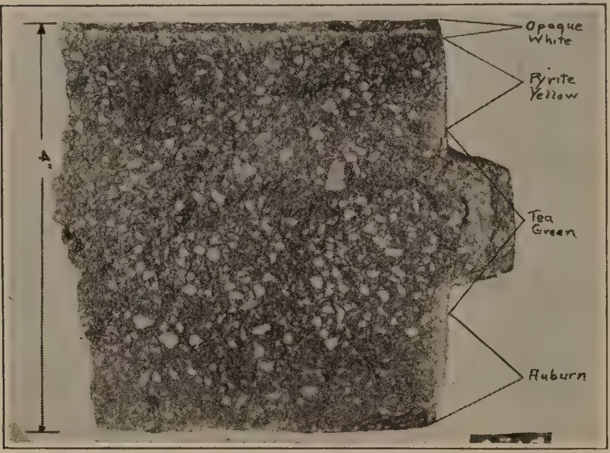

FIG. 1.—Cross-section of a silica shape used in construction of Semet-Solvay ovens for By-Product Coke Corp., S. Chicago, Ill.

Description of Samples

The first shipment tested consisted of brick produced from Baraboo ganister in the Chicago district. They had been used in a horizontal flued oven with an operating temperature probably up to 2650°F. These samples were assigned letters A, B, and C. The second set of brick had been made from Alabama quartzite in the Birmingham district and had been used in a vertical flued oven with an operating temperature probably up to 2600°F. They were assigned letters D, E, and F. Both samples of brick had been in service for twelve years under constant operation.

FIG. 2.—Cross-section of Sample C.

The Chicago district shapes will be described first.

Sample A was a 4-inch block used in the oven wall with one surface exposed to the coal. The block had been placed in the oven in 1912 and removed in 1924. It was located 4 feet above the floor and 3 feet from the coke side end of the oven. Figure 1 shows a broken cross-section of the shape with the various colored bands indicated.[1]

Sample B was a block 2 inches thick used as an inside brick for the flue and was not exposed to the coal. There were two sections to this sample. The face exposed to the flame was opaque glass for $\frac{1}{8}$ inch. The balance of the shape was clay color with white spots scattered through this portion. This brick was placed in the oven in 1915 and was 4 feet from the floor and 3 feet from the coke side of the oven.

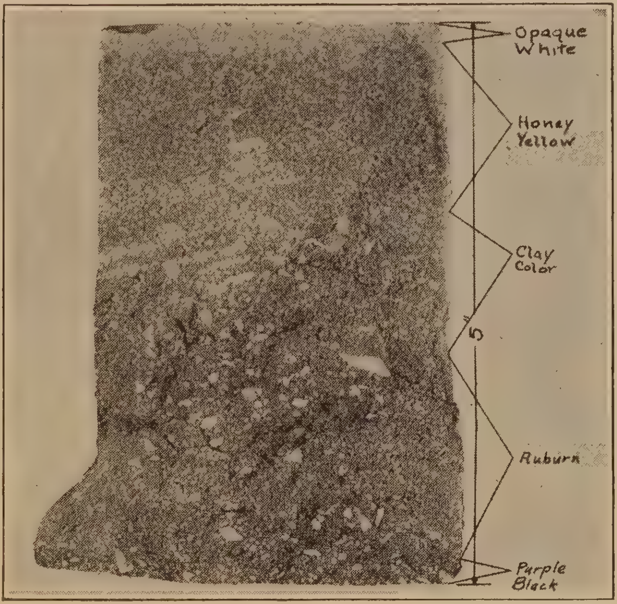

Fig. 3.—Cross-section of a silica shape used in construction of Woodward Iron Company, Battery No. 2, Brand 74–L.

Sample C was the same shape as Sample A, but had not been used. This block was part of the original shipment made in 1912. It was straw color with gray and white spots scattered through the brick. The size of grain to which the ganister had been ground is shown by a section of the brick, Fig. 2.

The Birmingham district samples are next described.

Sample D was a liner block used in the flue wall and was 5 inches thick. A section of this brick is shown in Fig. 3. This shape was located 2 feet 6 inches from the floor and 7 feet 6 inches from the coke side

Fig. 4.

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[1] The colors referred to in describing the brick were obtained by comparing the samples with a color chart in "Color Standards Nomenclature," by Robert Ridgway.

end of the oven. This shape was placed in the oven in 1913 and removed in 1925.

Sample E was another liner block located 4 feet 3 inches above Sample D in the same flue wall. The first ⅛ inch from the coal side was a purple black and the next 4 inches were a clay color with some white spots. The last inch was a honey color. This shape was placed in the oven in 1913 and removed in 1925.

Sample F was from the original shipment of shapes for the oven construction but was not used. These shapes were manufactured in 1913. The interior of the piece was cream color with gray and white spots of ganister. Figure 4 is a photograph of a broken section of the block, showing the spots and grain size. This piece was five inches thick.

Other samples were obtained but have not been described since the above shapes are representative.

Tests Performed and Results Obtained

Each colored zone was sampled separately and tested for:

1. Fusion
2. Apparent specific gravity
3. Per cent porosity
4. True specific gravity
5. Microscopic examination
6. Chemical analyses

The results obtained on the samples are as follows:

Sample No.	Section tested	App. sp. gr.	Per cent porosity	True sp. gr.	Fusion	Microscopic examination
A	Coke side 1½″*	2.319	20.93	2.321	31	Tridymite Cristobalite
	Flue side 1–2″	2.289	20.92		31	Tridymite Cristobalite
	Flue side ⅛″			2.294	31	Tridymite
B	Flue side 1″	2.288	21.0		30–31	Tridymite Cristobalite (slight)
	Wall side 1″	2.317	21.2		30–31	Cristobalite Tridymite
	Flue side 1½″			2.327	30–31	Cristobalite Tridymite
	Flue side ⅛″			2.282	31	Tridymite
C	Center	2.340	21.88	2.350	31–32	Quartz Cristobalite Tridymite(slight)

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* The distance was that measured from coke or flue side and sample was from that section contained in these limits.

Sample No.	Section tested	App. sp. gr.	Per cent porosity	True sp. gr.	Fusion	Microscopic examination
D	Flue side ¼–2½″				32	
	Flue side 1–1½″	2.284	25.51	2.309		Tridymite Cristobalite
	Coke side ¼″			2.298	30–31	Tridymite Cristobalite
	Coke side 1″	2.304	22.6	2.333		Cristobalite
	Flue side ⅛″			2.295	32	
	Coke side ¼–2″				32	
E	Center	2.275	22.42	2.287	31–32	Tridymite
F	Center	2.325	22.31	2.317	32	Quartz Cristobalite Tridymite

Various sections were analyzed for chemical constituents. The Al_2O_3, Fe_2O_3, CaO and MgO contents were determined by analysis but the SiO_2 values indicated were obtained by difference.

	A ¼–1 in. from flue side	A 1–2½ in. flue side	A ¼–1½ in. coke side	C Center
SiO_2	95.45	95.28	95.25	95.97
Al_2O_3	1.31	1.16	1.22	0.98
Fe_2O_3	0.91	1.16	1.12	0.95
CaO	2.25	2.32	2.32	2.00
MgO	0.08	0.08	0.09	0.10
	100.00	100.00	100.00	100.00

	D ¼ in. flue side	D ¼–2¼ in. flue side	D ¼ in. coke side	D ¼–2 in. coke side	F Center
SiO_2	96.62	96.48	93.77	96.16	96.19
Al_2O_3	1.12	0.67	2.56	0.80	1.01
Fe_2O_3	0.40	0.89	2.02	0.99	1.71
CaO	1.64	1.73	1.40	1.80	1.87
MgO	0.22	0.23	0.25	0.25	0.22
	100.00	100.00	100.00	100.00	100.00

Discussion of Results

The specific gravity values justify the assumption that the silica has been largely converted to tridymite during use. The original sample from the Chicago district contained unconverted quartz, but the specific gravity shows a change to tridymite and cristobalite. This was confirmed by the microscopic examination. The porosity has been little changed and the fusion point only slightly lowered. The chemical analyses show a slight increase in R_2O_3, probably due to coal ash coming in contact with the walls. The same difference was found in the silica brick from the Birmingham district. Long heat service causes the quartz to be converted to tridymite or cristobalite in the hotter or cooler zones of the brick. The increase in R_2O_3 is very definitely shown in the analysis of the $\frac{1}{4}$-inch coke side of Sample D. This sample was from the face of the shape next to the coal where the silica has combined chemically with the ash in the coal. This is well shown by the change in color of the silica on the surface of the brick. The face of the brick next to the flue was reduced in Fe_2O_3 content but increased in Al_2O_3 and in SiO_2. The color of the silica from both districts was about the same after the same length of service. The chemical changes were very slight except on the faces of the samples.

The unused brick showed quartz, cristobalite and tridymite in the mass. The amount of tridymite in Sample A was not as large as in Sample D. The silica at the flue face was practically completely converted to tridymite and the cristobalite increased as the cooler face was approached. In the case of Sample D "coke side 1" an occasional grain of quartz was found surrounded by cristobalite. This section evidently had not been heated to a high enough temperature to cause a complete inversion. The change of quartz to cristobalite and tridymite must have occurred at temperatures of 1000–1300°C since the coal face of the oven wall would not ordinarily exceed 1300°C. Evidently long time or a catalyst has bought about this change in the structure of the silica.

Summary

The following general conclusions have been reached:

1. Silica brick made from different quartzites have like properties after long service.
2. Very little change in chemical composition occurred.
3. Very slight change in porosity resulted.
4. The long service has brought about a conversion of the quartz to cristobalite and tridymite. On the flue face of the brick chiefly tridymite was present while on the coke face cristobalite was predominant.
5. The silica brick were in good condition after twelve years of continuous service at operating temperatures probably as high as 2500-2600°F. The only vitrification which had occurred was a glazed surface on the flue face.

The author wishes to acknowledge the assistance which J. A. Shaw has given in determining the analyses of the samples.

CHEMICAL COMPOSITION OF WINDOW GLASS[1]

By Edwin P. Arthur

ABSTRACT

The compositions of window glasses manufactured by various methods are compared. The tendency of glass to devitrify and ways of overcoming this are discussed, using diagrams based on the work of Morey and Bowen to illustrate the various points.

The ideal window glass composition, of course, is that one which will meet the market demand and which can most readily be manufactured at a profit. The manipulation of machinery used to make sheet glass permits some variation in the chemical composition. The glass forming machine, however, cannot accommodate variations in physical characteristics as did the workmen who made window glass by "hand." Consequently a much more uniform melt is required for best operation of the glass making machines than was ever necessary for "good glass" in a "hand plant."

One of the prime requirements of window glass is durability, stability or resistance to weathering. Gelstharp and Parkinson[2] have pointed out the possible composition of glass of three components SiO_2, CaO, and Na_2O on the basis of durability. The composition limits are indicated in the triaxial diagram (Fig. 1) by the shaded area. It is understood that minor constituents such as iron, alumina in small quantity, sulphates, chlorides, etc., would affect the behavior of commercial glass to some extent.

Method of manufacture	1 Hand-made	2 Lubbers	3 Slingluff	4 Colburn	5 Fourcault
SiO_2	71.9	74.3	73.1	72.8	73.8
CaO MgO	14.2	12.6	14.2	13.1	11.1
Na_2O	13.9	13.1	12.7	14.1	15.1

The number dots within the shaded area in Fig. 1 refer to the table, which shows the approximate composition of five window glasses manufactured in different ways. The percentages in the table were calculated from typical analyses of glasses by deducting the total of minor constituents from 100% and recalculating the percentage of silica lime and alkali of the remainder. The best present practice

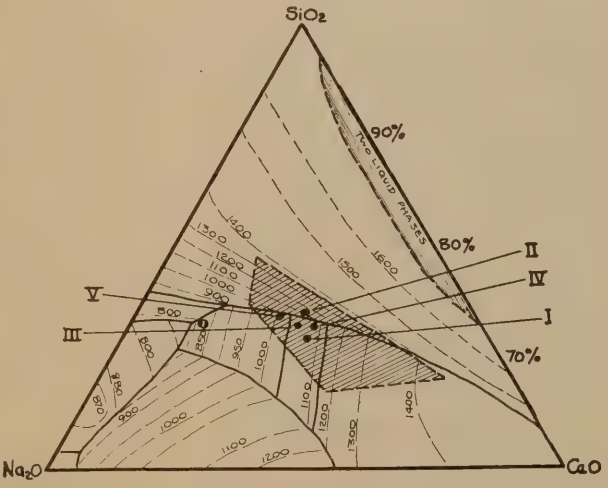

FIG. 1

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb. 1926 (Glass Division). Received January 8, 1926.

[2] *Trans. Amer. Ceram. Soc.* **16**, 109 (1914).

for window glass composition would seem to fall in a rather limited field. The different glasses are, nevertheless, distinct from each other as the glass making machines are sensitive to a surprising degree.

One of the principal manufacturing difficulties, especially with the Colburn and Fourcault machines, arises from a tendency of the glass to devitrify. If glass is cooled to reach a proper viscosity for working, some component of the melt may crystallize introducing opaque masses into the sheet thus forming highly objectionable defects.

Recent work of Morey and Bowen[1] is extremely interesting in this connection. They determined the crystallizing points of the three component system SiO_2, CaO, Na_2O by a series of fusions and quenchings employing special technique for accuracy. Their results, shown in Fig. 1, set the temperature limits very definitely beyond which devitrification will take place, disregarding the effect of minor constituents which may be in commercial glass as above.

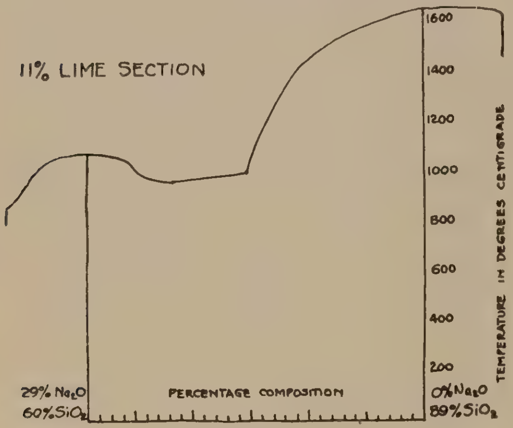

FIG. 2

In Fig. 2 is shown a two-component section through the Morey-Brown diagram at the line of 11% CaO. It is readily seen that the composition for a durable glass which can be cooled to the low point without devitrification is about 15% Na_2O and the minimum temperature about 1000°C, facts entirely confirmed by practice. For example, such a glass as mentioned will work well at 993°C while a variation of 10° is known to cause considerable difficulty. It is seldom that the results of so-called pure research so exactly coincide with practice. The many factors entering into large scale operation often vitiate or mask the most thoroughly accurate work of this character.

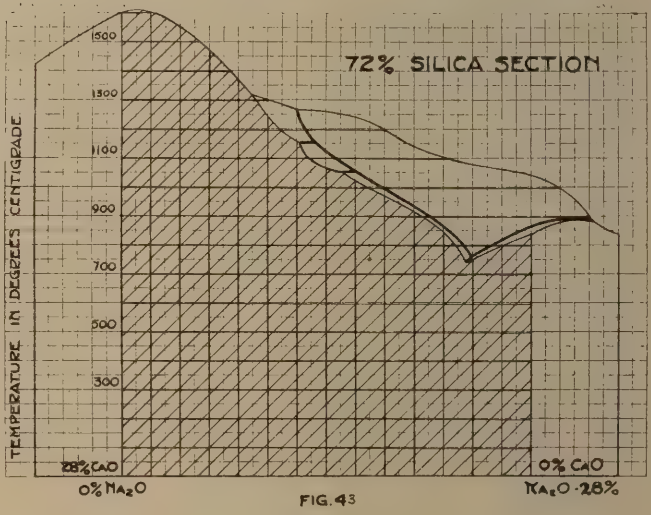

FIG. 3

A two-component section at 72% SiO_2 is shown in Fig. 3. A glass such as the hand made window glass No. 1, containing 14% CaO and 72% SiO_2 is generally worked and quickly cooled from temperatures near 1150°C (2100°F). This temperature is well above the crystallization point, a fact which explains the absence of devitrification troubles in making hand blown glass.

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[1] *Jour. Soc. Glass. Tech.* **9,** 226 (1925).

The author wishes to acknowledge helpful criticism of James R. Withrow of the Department of Chemical Engineering, Ohio State University, and aid of W. H. de Bruin in preparation of drawings.

COLUMBUS, OHIO.

THE HEAT REQUIRED TO FIRE CERAMIC BODIES[1]

By A. Ernest MacGee[2]

ABSTRACT

A differential thermal method for determining interval specific heats of ceramic materials is described. The specific heat of the unknown is determined by comparing its temperature to that of quartz after each sample has been subjected to a definite heat treatment. This method shows the number of calories required to heat one gram of the material in question from 0 to *t*°C, accounting for all thermal processes which the material may undergo during the heating process. It shows the temperatures at which the various thermal processes begin and end as well as the quantitative figures for the more pronounced of these thermal processes.

The kaolin, ball, flint, and diaspore clays undergo an endothermic reaction at about 575°C which amounts to "60 to 130" calories per gram of the air dried material. They undergo an exothermic reaction at about 960°C which amounts to about 25 calories per gram of the air dried material. About 510 calories are required to heat one gram of any firebrick body from 25 to 1200°C, the specific heat over this interval being about .43. About 500 calories are required to heat one gram of any kaolin or ball clay from 0–1000°C, the specific heat over this interval being about .5. About 290 calories are required to heat one gram of flint or feldspar from 0–1050°C, the specific heat over this interval being about .28.

Instead of the kiln efficiencies being about 22% as was previously believed, this work proved them to be about 35%.

Introduction

1. Purposes of Investigation

The present investigation was undertaken with the object of ascertaining the number of calories necessary to heat a given mass of a ceramic body to any given temperature. This involved the determining of the interval specific heats of the various materials. By interval specific heat is meant the number of calories per degree which must be added from some external source in order to raise the temperature of one gram of material from 0 to *t*°C.

The determination of the interval specific heats of most ceramic materials is greatly complicated owing to the fact that they often undergo thermal changes on heating which are not reversed on cooling, such as the decomposition of carbonates, sulphates, hydrates, etc. In addition to the thermal processes accompanying the various chemical reactions, there are often physical reactions that involve thermal changes, such as the transformation of one allotropic modification into another, the latent heat of fusion, and the solution of solid constituents by a melt. F. Richars[1] has pointed out that the specific heat near the fusion point is abnormally high, being due to the fact that, to a great extent, the latent heat of fusion is involved. Furthermore, many ceramic materials such as the clays contain combustible matter which is fired out during the firing process. Therefore, air must be in free contact with the sample under test so as to permit this combustion to take place. Any method employed for the determination of the interval specific heats of ceramic bodies must be of such a nature as to account for any and all thermal changes which the material may undergo in heating. This is true because the amount of heat required to be added to heat a given body to a given temperature is dependent upon the net result of all endothermic and exothermic reactions which the material undergoes during the heating process. Since none of the methods previously employed accounted for all of these various thermal processes, it was necessary either to revise one of the old methods or develop a new one. A method was developed which, it is believed, covers all of the conditions underlying interval specific heat determinations when applied to materials which undergo irreversible thermal changes. In addition to determining the number of calories required to heat a given weight of material to *t* degrees centigrade, it was possible to derive the actual quantitative values for the more pronounced thermal processes which the material undergoes. Also, the temperatures at which the reactions take place are plainly discernible.

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[1] This investigation was carried out coöperatively by the U. S. Bureau of Mines and the Ohio State University Engineering Experiment Station, and the data herein given has been presented through the Department of Ceramic Engineering to the Graduate School at the Ohio State University as a thesis in partial fulfillment of the requirements for the Doctor's degree. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (General Session.) Received January 12, 1926.

[2] Research Engineer, U. S. Bureau of Mines.

2. The Problem of Heat Economy

The problem of heat economy in the ceramic industries is, quite obviously, of very great importance because of the large consumption of fuel in the drying and firing operations, ranging from 10 to 30% of the total cost of production in the different industries. Anything that would lead to a lessened fuel consumption would greatly benefit the ceramic industries. A variety of drier and kiln constructions, such as the tunnel car and continuous kilns, has been designed to obtain greater economy of fuel. Recommendations for improving the designs of kilns and firing methods can be scientifically made only when the fundamental data, such as thermal conductivity, specific heat, convection, radiation, and heat distribution, which are connected with the drying and firing operations, are known. Much of these essential data, especially interval specific heats, is lacking.

A. V. Bleininger[2] conducted an investigation to ascertain the distribution of heat in several ceramic kilns. This investigation covered four different kilns, two of which were firing terra cotta; the other two were firing paving brick and sewer pipe respectively. The heat required to heat one gram of a clay containing 2% of hygroscopic and 7% of chemical water from 20 to 1120°C was calculated to be distributed as follows:

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[1] "Die Theorie des Gesetzes von Dulong und Petit," *Z. f. Anorg. Chem.*, **59** (1908).

[2] "A Study of the Heat Distribution in Four Industrial Kilns," *Trans. Amer. Ceram. Soc.*, **10**, 412–49 (1908).

Used in driving off hygroscopic water	12.1 cal.
Used in driving off chemical water	23.1 cal.
Used in heating dry clay (sp. ht. assumed to be 0.2)	204.6 cal.
Total	240.8 cal.

From considerations similar to these it was determined that of the total heat inducted into the kilns 5.71% was used to heat the sewer pipe, 11.3% to heat the paving brick, and 12.51% and 8% respectively of the total inducted heat was used to heat the terra cotta.

During the years 1922 and 1923, the U. S. Bureau of Mines[1] investigated the heat used in several types of kilns employed in firing refractories. This investigation involved an extensive series of experiments which were conducted in the respective factories under actual operating conditions and furnishes, therefore, an interesting and significant insight into the actual distribution of heat during the firing process. The utilization of heat was found to be distributed among several sources as follows:

1. Heat used to raise the temperature of the brick to the finishing temperature (calculated from an interval specific heat of about 0.26).
2. Heat used to evaporate the water from the ware.
3. Heat lost as combustible matter in the ash.
4. Heat lost as combustible matter in the flue gases.
5. Heat lost in dry flue gases.
6. Heat lost in water vapor in flue gases derived from coal.
7. Heat used to raise the temperature of the walls of the kiln.
8. Heat used to raise the temperature of the crown of the kiln.
9. Heat lost by radiation and convection from the crown and walls of the kiln.
10. Heat given up by gases between the bottom of the kiln and the stack.

The quantitative distribution of the heat as calculated from the experimental data is shown in Table I.

Since in many cases, the unaccounted for losses of heat go as high as 20%, it is apparent that there is room for a substantial increase in the accuracy of some of the experimental data from which the values for the distribution of heat was calculated. The value used as representing the interval specific heat of the fire brick was about 0.26. This value represents the specific heat of the fired brick and is, in all probability, entirely too low for the green brick. The interval specific heats of the green brick were determined by the method employed in this investigation and found to be about 0.43 over the interval 0–1100°C. This obviously greatly reduces the unaccounted for heat losses and materially increases the efficiency rating of the various kilns.

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[1] W. E. Rice and R. A. Sherman, "Determination of the Distribution of Heat in Kilns Firing Clay Wares," *Jour. Amer. Ceram. Soc.*, **7**, 738–63 (1924).

Thus, one sees that only a portion of the heat produced by the fuel is utilized in actually heating the ware to its maturing temperature. If the interval specific heat of the material to be fired is known, the amount of heat actually required to heat it to its maturing temperature can be readily calculated; that is, the efficiency of a kiln operation can be accurately determined simply by knowing the calorific power and quantity of fuel consumed in heating the kiln of ware of known interval specific heat to its maturing temperature.

3. Methods for Determining Specific Heats

The procedures which have been employed in the past to determine the specific heat of a given material can be classified under one or more of the following general methods:

(*a*) From calculations based upon the law of Dulong and Petit and which require no experimental determinations. This law states that the product of the specific heat and the atomic weight of the solid elements is constant, being approximately 6.4.

(*b*) From data obtained by a method based on Newton's law of cooling, which states that the time taken by equal masses of substances under exactly identical conditions in cooling through equal ranges of temperature is directly proportional to their specific heats.

(*c*) From data obtained by the procedure known as the method of mixtures. This involves heating the weighed unknown to the temperature in question and allowing it to fall into a calorimeter. Thus the quantity of heat it contains at the time of dropping can be measured and its specific heat calculated.

(*d*) From data obtained by measuring the electrical energy required to heat the sample to a given temperature, the current passing through the test piece. This method is, unfortunately, limited to conductors of the first class and is thereby inapplicable for measuring specific heats of ceramic materials.

(*e*) From data obtained by measuring the energy required to bring the material, contained in a calorimeter, to a given temperature. Griffiths and Griffiths[1] were probably the first to measure the heat required to elevate a sample to a given temperature by noting the electrical energy consumed in the process. Thus knowing the number of calories absorbed by a given weight of sample in heating it to t°C, its specific heat is readily calculated. They used a twin calorimeter, one of which contained the sample. The calorimetric method in one modification or another, has been used by many investigators for ascertaining specific

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[1] Griffiths and Griffiths., *Phil. Trans. Roy. Soc. of London*, **A213**, 119 (1913).

TABLE I

HEAT ACCOUNTS OF REFRACTORY KILNS

Type of kiln	Inside dimensions (feet)	Number of furnaces	Grates	Number of stacks	Ware	Pounds of coal per thousand 9-in. equiv. for a no. of preceding firings	Test	Test serial number	Duration in hrs.	Final temp. in °F	Pounds of coal per 9-in. equiv.	Tons of coal per T. of ware	Per cent total heat in coal fired
Round downdraft	20	10	Horizontal	1	Fire clay	——	*A*	1	149½	2140	1270	0.20	100.0
							B	2	117	1980	1390	0.22	100.0
Rectangular downdraft "Newcastle"	30½x16½	6	Horizontal	1	Fire clay	1875	*A*	3	156	2140	1730	0.25	100.0
							B	4	134½	2230	1700	0.24	100.0
Round downdraft	30	12	Sloping	1	Fire clay	2180	*A*	5	206½	2160	1940	0.28	100.0
							B	6	129	2210	1510	0.22	100.0
Round downdraft	28	8	Sloping	1	Fire clay	1200	*A*	7	154½	2110	980	0.14	100.0
							B	8	114	2220	1070	0.15	100.0
Round downdraft	25	10	Dead bottom	1	Fire clay	1513	*A*	9	83½	2150	1420	0.20	100.0
							B	10	80	2100	1370	0.20	100.0

TABLE I (*concluded*)

HEAT ACCOUNTS OF REFRACTORY KILNS

Heat used to raise the temperature of brick	Heat used to evaporate moisture from brick	Heat in combustible ash	Heat in combustible flue gases	Heat in dry flue gases	Heat in water vapor in the flue gases formed from coal	Heat used to raise the temperature of the walls of the kiln	Heat used to raise the temperature of crown of kiln	Heat lost by radiation and convection from the walls of the kiln	Heat lost by radiation and convection from the crown of the kiln	Heat given up by gases between bottom of kiln and stack	Unaccounted for losses obtained by difference	Test serial number	Unaccounted for losses obtained by difference using specific heat values obtained in this investigation
Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent		
19.4	3.5	7.5	1.5	27.4	5.0	15.3	3.9	2.2	0.7	5.6	8.0	1	– 4.7
15.7	3.2	6.8	0.0	24.8	4.7	12.3	3.0	1.2	0.5	13.0	14.8	2	4.3
16.5	0.4	6.3	0.3	31.0	5.5	6.0	2.1	2.9	6.5	11.9	10.6	3	0.3
17.3	0.4	5.0	0.6	31.1	5.5	6.9	2.1	1.9	5.5	7.5	16.2	4	4.9
16.6	1.4	4.2	5.3	19.3	6.1	5.5	2.1	1.0	4.4	10.7	23.4	5	13.1
23.6	1.6	4.2	2.1	18.3	6.1	7.3	2.8	0.5	4.0	6.7	22.8	6	8.2
26.3	2.0	3.6	0.5	20.4	4.7	8.2	3.1	2.0	4.4	12.2	12.6	7	– 3.5
27.7	2.0	4.7	0.3	18.8	4.9	8.2	3.4	0.7	3.8	12.3	13.2	8	– 3.3
23.8	1.2	4.5	0.5	21.2	5.6	6.7	3.6	1.2	1.0	12.0	18.7	9	5.2
22.0	1.0	6.4	0.6	18.5	5.4	6.8	3.4	0.5	0.7	5.1	29.6	10	17.0

heats and thermal reactions which a sample undergoes during a heating process.

(*f*) From data on heat required to bring the material to a given temperature, calculated from curves obtained by a differential thermal method.

Previous Investigations

Joseph Black[1] was probably the first to illustrate the different capacities for heat of the same mass at different temperatures. The work of Black was continued by Irvine[2] who was the first to publish a clear explanation disentangling the four entities, specific heat, mass, temperature change and quantity of heat, when more than one was varied at a time. This work was conducted about 1770, and from then on the scientific world has had a clear conception of the phenomenon which enables different substances and the same substance at different temperatures to absorb different quantities of heat. The work of Irvine was followed by that of Laplace and Lavoisier.[3] Although Crawford[4] was probably the first to use the method of mixtures, Dulong and Petit[5] employed it to make the first really accurate specific heat measurements and, as a result of their determinations, formulated their well-known law. This work was followed by that of Potter,[6] Regnault,[7] Richards and Frazier[8] and others. Wilson, Holdcroft and Mellor[9] determined the specific heat of fire brick by a modification of the method of mixtures and found the average value to be 0.261 at 1150°C. They found that the specific heat equals $.193+.00006\ t$. Doughill, Hodsman and Cobb[10] found the specific heats of fireclay brick and silica brick to be 0.26 and 0.27 respectively at 1000°C. These values agree quite favorably with those of Bradshaw and Emery[11] who found the specific heats of Stourbridge fire brick and silica brick to be 0.263 and 0.262 respectively at 1000°C. Heyn, Bauer and Wetzel[1] made quite an extensive investigation into the heat conductivities and specific heats of various ceramic materials in the fired state. They found the mean specific heat of fire brick to be .236 over the interval 20–600°C and .263 over the interval 20–1200°C. In addition to the previous citations, Green,[2] Steger,[3] Magnus,[4] Tadokoro,[5] Wietzel,[6] Knote,[7] and others have determined specific heats for a variety of ceramic materials and bodies by using the method of mixtures.

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[1] J. Robinson, "Lectures on the Elements of Chemistry," edition of 1807, Philadelphia; p. 81. Note 1 by Robinson, p. 330.

[2] Irvine, "Essays, Chiefly on Chemical Subjects," London, 1805.

[3] Memoirs de L'Academie de Science, 355 (1780), Oeuvres de Lavoisier, II, 287, 724 (1862).

[4] Experiments and Observations on Animal Heat, London, 1777–78.

[5] *Ann. de Chem. et de Phys.* [2], **7,** 142 (1817); *Ann. de Chem. et de Phys.* [2], **10,** 395 (1819); *Jour. Ecole Polytechnique,* **11,** 189 (1820).

[6] *Edinburgh Jour. Sci.* (New Series), **5,** 80 (1831); **6,** 163 (1832).

[7] *Ann. de Chem. et de Phys.* [2], **73,** 5 (1840); *Ibid.* [3], 322 (1843); etc.

[8] *Chem. News,* **68,** 84 (1813).

[9] "The Specific Heat of Fire Brick at High Temperature," *Trans. Ceram. Soc.* (Eng.), **12,** 279–84 (1912–13).

[10] "The Thermal Conductivity of Refractory Materials," *Jour. Soc. Chem. Ind.*, **34,** 465–71 (1915).

[11] "Specific Heat of Refractory Materials at High Temperatures," *Trans. Ceram. Soc.* (Eng.), **19,** 84–92 (1919–20).

White[8] carried out a very extensive series of experiments on silicate specific heats. This method consisted of a very refined modification of the method of mixtures, every precaution being taken to eliminate errors. By virtue of Dr. White's extensive experience in calorimetric work, his values for the specific heat of quartz can be looked upon as being the most accurate available in the literature. Table II shows the average values he obtained for the various materials experimented with and Fig. 1 gives a graphical illustration of the average values for quartz.

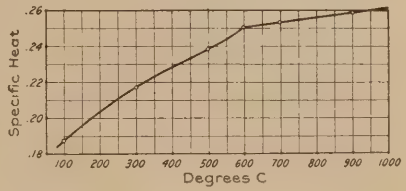

Fig. 1.—Showing the specific heats of quartz according to Walter P. White's data.

The method of mixtures in one modification or another and the method based on Newton's law of cooling have been used in the past almost exclusively for the determination of specific heats. Both of these methods are based upon the fundamental assumption that any thermal effects which take place on heating are reversed on cooling. It has long been known that most of the materials employed in the compounding of ceramic bodies undergo various thermal changes on heating which are not reversed on cooling and, lately, considerable effort has been expended in trying to develop a method for specific heat determinations which would account for these irreversible thermal changes. With this in view, Navias[1] used a calorimetric method in which a measured amount of electrical energy was applied to the calorimeter. By measuring the amount of electrical energy needed to heat the empty calorimeter to a given temperature and likewise, measuring the amount of electrical energy needed to heat the calorimeter with the sample in place, it is evident that any difference must be the sum total of heat absorbed or evolved by the sample. Using this method, it was possible for the first time to give correct values for the interval specific heats of ceramic materials which undergo irreversible thermal changes. The values obtained by Navias showed the interval specific heats of raw clays to be about twice as great as had ordinarily been supposed. Unfortunately, in order to avoid heat losses which would have made the errors in a determination excessively large, it was found necessary to carry out the experiments in vacuo. This, of course, precluded the method for the determination of the values most urgently desired because it was not applicable for materials containing combustible matter. However, the method can be easily modified so as to permit a controlled atmosphere around the sample and, if so done, would then be applicable to the cases involving oxidizable materials. Table III shows the interval specific heat values obtained by Navias for the materials in question.

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[1] "Untersuchungen über die Wärmleitfahigkeit feuer fester Baustoffe," *Mitteilungen aus dem Königlichen Materialprüfungsamt*, **32,** 89–199 (1914).

[2] A. T. Green, "The Specific Heat of Magnesite Brick at High Temperatures," *Trans. Ceram. Soc.* (Eng.), **22,** 393–97 (1922–23).

[3] Steger "The Specific Heat of Refractory Materials," *Silikat Z.*, **2,** 203 (1914).

[4] A. Magnus, "Messungen spezifischer Warmerfester Korper die hohen Temperaturen," *Physik Zeitschr.*, **14,** 5–11 (1913).

[5] Y. Tadokoro "On the Determination of the Thermal Conductivity, Specific Heat, Density and Thermal Expansion of Different Rocks and Refractory Materials," Tohoku Imperial University, *Science Reports*, 1st Series, Mathematics, Physics and Chemistry, **10,** 339–410 (1912).

[6] R. Wietzel, "Die Stabilitatsverhaltnisse der Glas und Kristallphase des Siliziumdioxydes," *Z. f. Anorg. Chem.* **116,** 71–95 (1921).

[7] Knote, "Note on the Specific Heat of Clay," *Trans. Amer. Ceram. Soc.*, **14,** 394–98 (1912).

[8] W. P. White, "Silicate Specific Heats," *Amer. Jour. Sci.*, **47,** 1–43 (1919); "Specific Heats of Silicates and Platinum," *Amer. Jour. Sci.*, **28,** 334 (1909).

TABLE II

SPECIFIC HEATS OF SILICATES FROM 0–t°C (White)

Temp.	Quartz	Cristobalite	Anorthite	Albite	Microcline	Wollastonite	Diopside	Amphibole	Pseudo Wollastonite
100	.1868	.1883	.1902	.1948	.1871		.1924	.2033	.1844
300	.2168	.2334	.2143	.2204	.2108		.2164	.2298	.2045
500	.2379	.2426	.2297	.2364	.2261		.2314	.2461	.2171
600	.2511								
700	.2543	.2509	.2399	.2474	.2371	.2274	.2421	.2576	.2259
900	.2596	.2569	.2481	.2561	.2451	.2344	.2500	.2661	.2324
1100	.2641	.2625	.2551	.2630	.2511	.2401	.2563	.2731	.2379
1160						.2416			.2394
1300		.2663	.2629						.2426
1400		.2680	.2674						.2448

It will be observed that there is a marked heat absorption up to about 900°C, after which there is in three of the samples, apparently, a very large heat evolution between 900 and 1200°C. This heat evolution is especially marked in the case of the A-1 English china clay and the North Carolina kaolin. These thermal changes are, obviously, not accounted for by the method of mixtures as is evidenced by the fact that the values obtained by Knote,[1] who used this method, are less than half as great as the above values for the same general class of materials.

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[1] L. Navias, "Measurement of the Heat Absorbed and Evolved by Clays during Firing and Cooling," *Jour. Amer. Ceram. Soc.*, **6** [12], 1268–98 (1923).

The next series of experiments undertaken with the object of measuring the interval specific heats of ceramic materials was made by Cohn,[2] who used a differential thermal method entirely different from any hitherto used for specific heat determinations. This method was based upon the behavior of the sample under a definite heat treatment as compared to that of a sample of known specific heat. The reference material used was one of the fired fireclay bodies that had been investigated by Heyn, Bauer and Wetzel.[3] Considerable errors are inherent in this method because of the fact that the final calory-temperature curve is obtained by combining several other curves. It fails more or less to account for the oxidation reactions because of the fact that the sample was placed in a platinum crucible which would, at best, permit only a limited oxidation. In all probability, the greatest error in connection with his procedure lies in his choice of the weight of sample to use. He used about two grams of material in each case. The author has found that, for material undergoing a thermal change, there is a definite weight which will give the greatest thermal effect. That is, Cohn could have varied his sample weight considerably in some cases without changing the value of the temperature-difference time curve. Table IV shows the values obtained by Cohn for the interval specific heats of the various materials he investigated.

TABLE III

HEAT ABSORBED IN CALORIES PER GRAM PER DEGREE ON HEATING AIR-DRIED (110°C) SAMPLES OF CLAY OVER THE TEMPERATURE RANGES GIVEN (Navias)

Temperature range °C	N.C.kaolin	A-1 English china clay	Tenn. ball clay	Raw flint clay
25– 420	0.49	0.42	0.47	0.47
420– 900	0.69	0.95	0.53	0.68
900–1200	0.23	0.075	0.51	0.24
25–1200	0.50	0.55	0.51	0.50

At this point it is undoubtedly pertinent to ask, aside from the investigations of Cohn and Navias, what evidence we have that

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[1] *Loc. cit.*

[2] W. M. Cohn, "The Problem of Heat Economy in the Ceramic Industry," *Jour. Amer. Ceram. Soc.*, **7** [5, 6, 7], 359–76, 474–88, 548–62 (1924).

[3] *Loc. cit.*

TABLE IV

MEAN SPECIFIC HEAT IN THE INTERVAL 20 to t°C (Cohn)

Temperature	Zettlitz kaolin	China clay	Artificial corundum	Sillimanite	Feldspar	Rose quartz	Norwegian quartz	Hohenbaca sand	Cristo-balite	Chalcedony	Green porcelain	Fired porcelain	Green stoneware	Fired stoneware	Halle clay	Green chamotte	Fired chamotte	Green porcelain glaze	Fired porcelain glaze
100	.201	.200	.203	.161	.161	.190	.190	.190	.194	.167	.185	.189	.181	.186	.189	.191	.197	.170	.179
200	.203	.202	.211	.161	.162	.205	.206	.205	.212	.172	.187	.195	.183	.192	.195	.194	.202	.174	.181
300	.213	.213	.223	.163	.168	.215	.217	.214	.237	.175	.197	.203	.192	.203	.211	.204	.213	.182	.189
400	.226	.226	.231	.167	.179	.226	.226	.223	.238	.177	.213	.212	.201	.212	.223	.211	.220	.193	.197
500	.249	.248	.242	.170	.191	.239	.239	.233	.244	.185	.228	.222	.215	.223	.248	.232	.231	.208	.199
600	.415	.415	.231	.173	.202	.256	.256	.251	.248	.189	.332	.232	.292	.234	.348	.347	.238	.247	.202
700	.430	.438	.239	.174	.211	.257	.257	.254	.252	.193	.324	.245	.289	.275	.344	.331	.244	.238	.204
800	.426	.424	.272	.175	.222	.259	.260	.257	.257	.198	.318	.264	.279	.286	.331	.311	.251	.259	.211
900	.438	.439	.287	.172	.229	.262	.263	.262	.261	.203	.324	.287	.281	.296	.323	.322	.260	.278	.218
1000	.428	.429	.304	.175	.246	.267	.267	.267	.226	.210	.331	.304	.289	.307	.344	.343	.277	.280	.230
1100	.422	.429		.195	.260					.218	.354	.337	.311	.324	.358	.365	.288	.290	.245
1200	.415	.416		.199	.262						.363		.328		.369	.384		.299	
1300	.406	.407		.205							.373		.340			.402		.307	
1400	.410	.412		.202							.383					.415		.292	

clays and other ceramic materials undergo thermal changes and, if they do, what is the extent of these thermal processes? The thermal phenomena occurring in clays on heating were first examined by H. le Chatelier[1] in 1887. This preliminary survey has since been extended and elaborated upon by a number of investigators. They observed accelerations and retardations in the rate of heating of the various clays. Mellor and Holdcroft[2] determined from time-temperature curves, obtained by a differential thermal method, that kaolinite underwent an endothermic reaction just above 500°C, continuing until a maximum was reached at about 650°C. Exothermic reactions took place at about 800, 900, and 1000°C. In the case of china clay, the endothermic reaction amounted to 42 calories per gram. The exothermic reaction at about 800°C, probably due to a polymerization of the alumina, amounted to about 21.5 calories per gram. Qualitative work along this line has been carried out by Rieke,[3] Ashley,[4] Wallach,[5] Satoh[6] and others; all of whom have shown that the various clays undergo enthodermic reactions in the neighborhood of 550°C and exothermic reactions in the neighborhood of 950°C.

Houldsworth and Cobb[7] and Sokoloff[8] in an extensive series of experiments on the effect of heat on clays, have shown that some water was lost at 100°C followed by an ever-increasing amount as the temperature was raised until it reached a maximum between 600 and 800°C after which there is practically no loss.

The Method

1. Theoretical Considerations

The method employed in this investigation is based upon the fundamental assumption that the change in temperature of any body is dependent upon its specific heat, its mass, and the quantity of heat added. This is summarized in the general equation:

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[1] H. le Chatelier, *Bull. Soc. Min.*, **10**, 207 (1887); *Z. Phys. Chem.*, **1**, 396 (1887).

[2] J. W. Mellor and A. D. Holdcroft, "The Chemical Constitution of the Kaolinite Molecule," *Trans. Ceram. Soc.* (Eng.), **10**, 94–120 (1910–11); **11**, 169–73 (1911–12).

[3] R. Rieke, "Einige Beobachtungen über den Gluhverlust von Kaolinen und Tieb," *Sprechsaal*, **44**, 637–40 (1911).

[4] H. E. Ashley, "The Decomposition of Clays, etc.," *Jour. Ind. Eng. Chem.*, **3**, 91–94 (1911).

[5] R. Wallach, *Compt. Rend.*, **157**, 48–50 (1913).

[6] S. Satoh, "A Study of the Heating and Cooling Curves of Japanese Kaolinite," *Jour. Amer. Ceram. Soc.*, **4**, 182–94 (1921).

[7] H. S. Houldsworth and J. W. Cobb, "The Behavior of Fireclays, Bauxites, etc., on Heating," *Trans. Ceram. Soc.* (Eng.), **22**, 111–37 (1922–23).

[8] A. M. Sokoloff, "Zur Frage des Molekularen Zerfalles des Kaolinits im Anfangs-Stadium des Gluhens," *Tonind. Ztg.*, **36**, 1107–10 (1912).

(1) $C=S\times t\times m$, in which

C = number of calories added

S = specific heat of the material

m = mass of the material

t = rise in temperature of the material

If the same number of calories be added to two different masses, m and m_2, of the same substance, the temperature of each mass will be directly proportional to the masses, m, and m_2, since their specific heats would be the same. However, if the same number of calories be added to two different masses, m, and m_2, of different substances, the temperature of each mass will not only be dependent upon the respective mass of each substance but will also depend upon the specific heats of the two substances.

Assume two different masses, m_1, and m_2, which are receiving heat. According to equation (1), one can write

$C_1=S_1\times t_1\times m_1$ and $C_2=S_2\times t_2\times m_2$, in which

C_1 and C_2 = number of calories added to each mass respectively

S_1 and S_2 = specific heats of m_1 and m_2 respectively

t_1 and t_2 = temperature of m_1 and m_2 respectively

If C_1 and C_2 are taken equal, one can write

$$S_1\times t_1\times m_1=S_2\times t_2\times m_2 \tag{2}$$

If S_1, t_1, m_1, t_2 and m_2 are known, S_2 can be readily calculated.

In the method employed in this investigation, there is the relation as expressed in equation 2. There are two weighed samples, m_1, and m_2, which receive the same number of calories and are so arranged that their temperatures can be measured. The specific heat, S_1, of m_1 is known from previous determinations. In order that the two samples may receive the same number of calories, each is placed in either of two identical platinum containers and suspended in a uniform temperature space of an electric furnace. Since the containers are of uniform size and in a uniformly heated area, it is assumed that the surface of each sample receives the same heat treatment. Each sample has a thermo-element inserted in it whereby its temperature is obtained. The reference sample is quartz of which the specific heat is accurately known from 0–1400°C. Thus, the conditions required by equation 2 are met and it is possible to calculate the specific heat, S_2, of the material under investigation. Through the kindness of Walter P. White, the quartz which was used as a reference material was the identical material used by him in his investigation into the specific heat of quartz and various silicates.

The assumption that, since both samples occupy the same volume in a uniform temperature area, they will each receive the same heat treatment and will, therefore, attain temperatures which are dependent upon their relative masses and specific heats, is more or less arbitrary.

The actual temperature that two samples so situated will attain is dependent upon several factors as follows:

1. The number of calories applied to each sample by radiation from the furnace walls, assumed in this case to be the same for both samples.
2. The mass of each sample.
3. The specific heat of each sample.
4. The reflecting and radiating power of the surface of each sample.
5. The granularity of the samples.
6. The transformations of a thermal nature which take place in the samples.
7. The heat conducted into or away from the samples by the thermocouple leads and the device used to suspend the samples in the furnace.
8. The thermal conductivity of the materials which compose the samples.

If the surfaces of all samples were the same, their reflecting and radiating power would be the same and could be disregarded. In order to meet this condition, either sample was placed in one of two platinum containers of exactly the same shape and size. In order to allow for the free play of air over the samples which is essential in order that the combustible and other oxidizable materials can be oxidized, each container was perforated by numerous small holes.

All samples were ground to the same general degree of fineness, namely, to pass a 100-mesh sieve. Therefore, any error attributable to this source is uniform for all determinations.

The suspension device and thermocouples were similar for both samples and a more or less uniform error is, therefore, introduced from this source. If the thermocouple leads were not insulated, heat would flow from the furnace into the wires and, as the temperature indicated is that of the junctions, the indicated temperature would not represent the temperature of the samples. In order to guard against this, the thermocouple leads were passed through a $\frac{3}{4}$-inch diameter "Sil-O-Cel plus clay" pyrometer protection tube, which also served to suspend the samples in the furnace.

The thermal conductivity of quartz is definitely known and provides the same factor in all experiments. The thermal conductivity of the various bodies and materials investigated is not necessarily the same and therefore introduces an error into all determinations. However, this error can be considered as being small because of the fact that the thermal conductivity of most ceramic materials hovers around a mean value. This is adequately shown by the work of Wologdine,[1] von

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[1] S. Wologdine, "Über das Warmeleitungsvermogen der feuerfesten Produkte," *Sprechsaal*, **33**, 454 (1908). "Untersuchungen über die Warmleitfahigkeit, Porosität und Gasdurchlassigkeit der feuerfesten materialen," *Sprechsaal*, **34**, 611–14 (1909).

Rinsum,[1] Brown,[2] Heyn, Bauer and Wetzel,[3] Green,[4] Doughill, Hodsman and Cobb,[5] and others.

Of course the thermal conductivity of the green clays is, in all probability, not the same as the fired material but, since these values are not known, the assumption is made that they are not radically different.

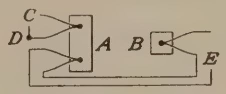

Fig. 2

A = neutral
B = sample
C and E = leads to millivolt meter
D = constant cold junction.

The scheme whereby the behavior of a sample undergoing heat treatment was ascertained by comparison with a neutral body was devised and first employed by Sir Roberts-Austen[6] who used it to determine the thermal behavior of the ferrous metals, using nickel as a reference body. Figure 2 shows a diagrammatic sketch of the thermocouple arrangement employed in this type of investigation.

Instead of using two distinct thermocouples for the determination of the temperature and temperature-difference of the samples as illustrated in Fig. 2, it was found preferable to use one thermocouple which had four junctions. This arrangement is shown diagramatically in Fig. 3.

Since the e.m.f. of a couple is dependent upon the difference in temperature of the two junctions, it is essential that one junction be constant in order to obtain comparable voltages. The cold junction was kept at 0°C by having it immersed in melting ice contained in a Dewar vacuum bottle. The thermocouples were calibrated by means of the method of fixed melting points, using metals of certified freezing point obtained from the U. S. Bureau of Standards. From the data thus obtained, a curve, Fig. 8, was drawn by plotting temperatures against millivolts.

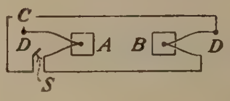

Fig. 3

A and B = samples (quartz and test)
D = constant cold junction
C = leads to millivolt meter.
S = switch

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[1] W. Von Rinsum, "Die Warmleitfahigkeit von feuerfesten Steinen bei hohen Temperaturen, u.s.w.," *Chem. Zentral.*, **2,** 94 (1919).

[2] G. Brown, "The Relative Thermal Conductivity of Silica and Clay Refractories," *Trans. Amer. Ceram. Soc.*, **16,** 382–85 (1914).

[3] *Loc. cit.*

[4] A. T. Green, "The Thermal Conductivity of Refractory Materials at High Temperatures," *Trans. Ceram. Soc.* (Eng.), **21,** 394–414 (1921–22).

[5] G. Doughill, H. J. Hodsman and J. W. Cobb, "The Thermal Conductivity of Refractory Materials," *Jour. Soc. Chem. Ind.*, **34,** 465–71 (1915).

[6] Sir Roberts-Austen, "Fifth Report to the Alloys Research Committee: Steel." *Proc. Inst. Mech. Engrs.* (British), 35–102 (1899).

Anyone familiar with curves will recognize that a curve of this type can be represented by the following equation:

(3) $E=at-bt^2$, in which t = temperature in degrees Centigrade
E = microvolts a and b = constants.

By determining E at two different temperatures, a set of simultaneous equations are obtained by means of which the constants, a and b, can be calculated. It was found that $E=9{,}700$ when $t=231.9$ and $E=27{,}400$ when $t=658.9$. Substituting these values in equation (3), we get

$$\begin{aligned}&(1)\ 231.9a-(231.9)^2b=9{,}700\\&(2)\ 658.9a-(658.9)^2b=27{,}400 \text{ or}\end{aligned}$$

$$\begin{aligned}&(1)\ 231.9a-53{,}777.6b=9{,}700\\&(2)\ 658.9a-434{,}149.2b=27{,}400\end{aligned}$$

multiplying (1) by 2.84, we get

$$\begin{aligned}&(1)\ 658.9a-152{,}782.2b=27{,}557.7\\&(2)\ 658.9a-434{,}149.2b=27{,}400\end{aligned}$$

substracting to eliminate (1) we get

$$\begin{aligned}658.9a-152{,}782.2b&=27{,}557.7\\658.9a-434{,}149.2b&=27{,}400.0\\\hline b&=.00056\end{aligned}$$

Substituting b in equation (1) we get

$$\begin{aligned}231.9a-(53{,}777.6).00056&=9{,}700\\a&=41.9577\end{aligned}$$

Thus the equation for the standardization curve of the thermocouple is

$$E=41.9577t-.00056t^2 \tag{4}$$

This is a quadratic equation. t can be calculated for any desired E. For example, the temperature, t, is calculated which corresponds to an E of 9,700. Rewriting equation (3), we get the following quadratic equation,

$$-bt^2+at-E=0$$

The formula for solving this equation is

$$t=\frac{-a\pm\sqrt{a^2-4bE}}{2b}$$

Substituting the values of the constants, a and b, and E in the above equation, we get

$$-t=\frac{-41.9577\pm(41.9577)^2-(4\times.00056\times-9{,}700)}{2(-.00056)}$$

$$t=\frac{-41.9577\pm(1760.3899-21.728)}{-.00112}\text{ or}$$

$$t=\frac{-41.9577\pm 41.6973}{-.00112}$$

and assuming plus to be correct, we get

$$t=\frac{-0.2594}{-0.00112}=231.91$$ degrees centigrade as the calculated temperature when E is 9,700.

It should be evident that t can be calculated with considerably greater precision than it can be read from a standardization curve.

Recalling that the differential thermocouple has the one junction inserted in the reference material quartz, and the other in the test sample, it is evident that this couple will not have a constant cold junction because the temperature of the furnace will be continually rising during an experimental run. Furthermore, if the test sample undergoes a very marked endothermic reaction, it may be as much as 100°C colder than the quartz at some particular temperature. However, this temperature will vary as the reaction becomes more or less intense. On the other hand, if the test sample undergoes an exothermic reaction, it may become much hotter than the quartz and, as before, this temperature will vary with the intensity of the reaction. In the first case, the junction inserted in the test piece would be the cold junction, usually a constantly varying cold junction, and as the test sample becomes the hotter, as in the second case, the junction inserted in the quartz becomes the cold junction. In other words, by employing a differential thermocouple, one is confronted with the situation of a constantly varying cold junction temperature. In addition to this, the temperature difference is continually varying. It is to be recalled that the e.m.f. generated by a thermoelement is not only dependent upon the difference in temperature but, also, upon the actual temperature of the two junctions. Evidently, if a differential millivoltage of 2.5 is obtained, its temperature equivalency could neither be calculated by equation (4) nor be determined by referring to the standardization curve of the thermocouple. It is impossible to do this because both the curve and the equation are based on the consideration that one of the junctions is constant, namely, maintained at 0°C. The question, then, is "can the exact temperature corresponding to any given e.m.f. generated by a differential thermocouple be determined." It can be accurately determined if the differential coefficient of E with respect to t is known. Referring to equation 3, $E=at-bt^2$; differentiating E with respect to t gives

(5) $$\frac{dE}{dt}=a-2bt,$$ in which

dE = the measured differential voltage.

dt = the differential temperature corresponding to dE
$a = 41.9577$
t = the temperature of one of the junctions
$b = .00056$

The temperature of one of the junctions is determined by the thermoelement inserted in the quartz which has a constant cold junction temperature of 0°C. Equation 5 can be written in the following form:

$$dt = \frac{dE}{a - 2bt}. \qquad (6)$$

Equation 6 is the working equation whereby the temperature differences are calculated. For example, the temperature is calculated which corresponds to a differential microvoltage of 200 when one of the junctions is at 203.2°C. Substituting the equivalents of the characters in equation 6, we get

$$dt = \frac{200}{41.9577 - 2(-.00056 \times 203.2) = 4.7°\mathrm{C}}$$

as the differential temperature which corresponds to a microvoltage of 200 at a cold junction temperature of 203.2 C. The temperature of the hot junction is, of course, 207.9° C.

Obviously, a differential microvoltage of 200 can correspond to as great a number of temperatures as there are values for t, which may be any number from zero to the extreme limit of the thermocouple. Unfortunately, many investigators who have used the differential thermocouple have taken the differential voltages to represent the same temperatures as the corresponding voltages when generated by a couple with a constant cold junction and have, therefore, introduced gratuitous errors into their work.

It was found expedient to take the temperature of the quartz at intervals of about 2.5 millivolts. As these readings were always taken at the same millivoltages, the corresponding values for t were calculated. Similarly, since t was constant in all cases, $a - 2bt$ would be the same for each experiment and was, therefore, calculated. This is in order to avoid their recalculation in all subsequent determinations. The values for t, $a - 2bt$, and the specific heat of quartz at the various temperatures are assembled in Table V.

The rate of heating was the same in all cases. Any errors attributable to these factors are constant.

The quantity of material which is used for each test piece is quite important and should be just sufficient to give the maximum thermal effect. This is evident from a consideration of the conditions incident upon an experimental determination. If the quantity of material be very small, it is easily conceivable that any thermal effect it may undergo would be lost owing to the extremely small amount of heat involved. The heat evolved or absorbed would be dissipated in the thermocouple wires or, from one cause or another, produce an effect totally imperceptible by the method employed to measure it. Evidently then, there must be sufficient material used so that any thermal effects will be of such magnitude as to be comparable to the sensitiveness of the method employed to measure them. On the other hand, it is not permissible to use more than the amount required to show the maximum thermal effect because these processes, whether chemical or physical, take place at a definite temperature regardless of whether there is one gram or one pound undergoing the change. This is necessary because the weight is used in the specific heat calculation.

2. General Method (Synopsis)

The materials to be tested were finely ground and a weighed sample placed in a small perforated platinum crucible. A similar crucible was filled with a weighed quantity of quartz. The two crucibles of material were placed in a uniform temperature zone of an electric furnace and the temperature raised to about 1050°C in about one hour. At arbitrarily chosen intervals, the temperature of each sample was measured by a chromel-alumel thermocouple imbedded in the material.

TABLE V

Millivolts	Temperature °C	Specific heat of quartz	$a - 2bt$
2.5	59.7	0.1823	41.874
4.5	107.1	0.1881	41.837
6.5	155.8	0.1963	41.783
8.5	203.6	0.2036	41.729
10.5	251.0	0.2104	41.676
12.5	299.4	0.2166	41.621
14.5	347.7	0.2223	41.577
16.5	396.5	0.2278	41.512
18.5	445.0	0.2326	41.459
20.5	494.0	0.2374	41.404
22.5	540.2	0.2425	41.352
24.5	590.3	0.2465	41.296
26.5	639.0	0.2499	41.241
28.5	687.0	0.2534	41.187
30.5	736.0	0.2553	41.133
32.5	785.3	0.2566	41.077
34.5	834.2	0.2579	41.022
36.5	883.0	0.2591	40.968
38.5	931.5	0.2604	40.914
39.5	956.1	0.2609	40.886
40.5	980.6	0.2615	40.858
41.5	1004.8	0.2620	40.832
42.5	1029.0	0.2626	40.806
44.5	1076.5	0.2636	40.751

3. Furnace The electric furnace consists of an alundum core 3 inches in internal diameter and 18 inches long wound with about 43 feet of 15 gage nichrome IV resistance wire. The core, made with especially thin ($\frac{1}{4}$ inch) and porous walls, has a pitch of 3 turns to the inch. Each end of the core is fitted into a Sil-O-Cel (90% Sil-O-Cel plus 10% ball clay) disk and made snug by forcing alundum cement into any cracks that existed. The disks are about 2 inches thick and of such diameter that they just fit into a double-walled iron cylinder 18 inches long. The inner wall of the iron cylinder is perforated with numerous small holes and the outer wall has four threaded openings into which are screwed $\frac{1}{2}$-inch iron pipes. The space between the alundum core and the iron cylinder is filled with coarse grog. The ends of the Sil-O-Cel disks are coated with a paste of sodium silicate and asbestos which forms an air tight joint between the furnace core and the iron cylinder. This compact unit is suspended in an iron cylinder 43 inches long and 18 inches in diameter by means of the four iron pipes which project through holes placed in the walls of the horizontal line of the cylinder. Thus when air is allowed to flow through the iron pipes, it passes into the space between the walls of the double-walled cylinder (the walls being sealed together at each end), through the holes of the inner wall into the loosely packed grog, and diffuses through the walls of the alundum core into the area in which is located the samples. This arrangement was adopted as being the most expedient method of introducing air into the furnace uniformly. However, it was found unnecessary to introduce excess air into the furnace in the cases investigated. Butted up against either end of the alundum core is a Sil-O-Cel cylinder 3 inches in internal diameter and 8 inches long. Either cylinder is suspended in the central line of the furnace by two asbestos disks 18 inches in diameter and 2 inches in thickness. A Sil-O-Cel end plug of about $2\frac{7}{8}$ inches external diameter and 12 inches long

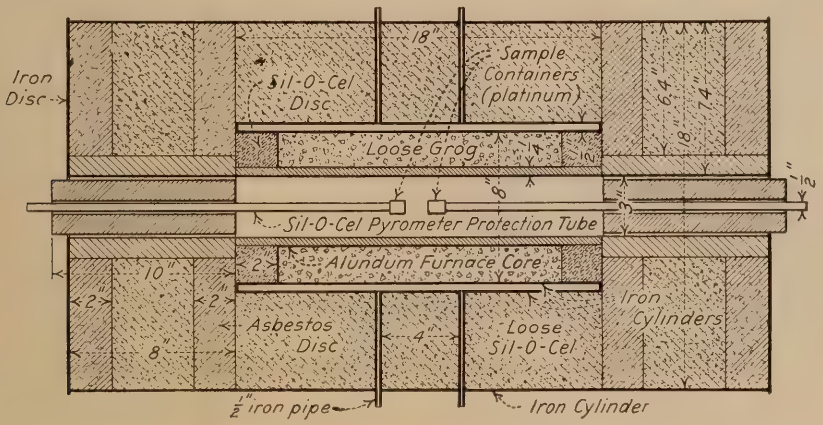

FIG. 4. Diagramatic cross-section through furnace, nichrome wire wound.

fits snugly into either of the Sil-O-Cel cylinders and against the furnace core. Each of the Sil-O-Cel plugs is pierced horizontally by a $\frac{7}{8}$-inch hole through which is inserted a Sil-O-Cel thermocouple protection tube 18 inches long and $\frac{3}{4}$ inch in diameter and so designed as to be capable of carrying two 22-gage thermocouple wires. The ends of the large iron cylinder are closed by means of a detachable iron cover plate. The space in the furnace not occupied by the above named materials is filled with loose Sil-O-Cel powder. The furnace, having a resistance of about 10 ohms, is heated by a 200-v. a.c. circuit. Figure 4 shows a diagrammatic sketch of a cross-section through the furnace.

4. Rheostat

A 300-ohm rheostat capable of carrying 30 amperes was used. The dial was equipped with a movable contact which could be so manipulated as to form 75 different contacts, giving ample flexibility in the speed of heating. The rheostat was so regulated as to obtain the same rate of heating in all experiments.

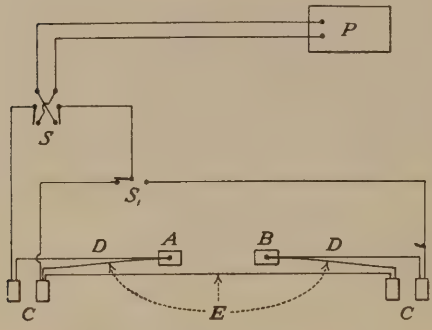

FIG. 5.

P = Potentiometer
C = Cold junctions (0°C)
E = Chromel thermocouple wire
D = Alumel thermocouple wire
A = Quartz
B = Sample
S_2 and S = switch

5. Sample Container

The sample containers consist of perforated platinum crucibles (150 perforations to the square inch) 2 cm. long and 1 cm. in diameter.

6. Temperature Measuring Equipment

The temperature of the test pieces as well as that of the reference material was ascertained by measuring the voltage developed by a No. 22 gage chromel-alumel thermocouple inserted in the materials under test. The high voltage adds considerably to the precision with which the temperature can be measured and this type of thermocouple is, therefore, preferable to a noble metal thermocouple for use in this investigation. The voltages developed by the thermocouples were determined by the potentiometer method, using the Brown precision potentiometer.

In the course of an experimental determination, it often happened that first the one and then the other of the two junctions of the differential thermocouple was hotter. This means that the current would flow first in the one direction and then in the other. Since the current must always flow into the potentiometer in the same direction, a double throw reversing switch is installed in the differential thermocouple circuit. Figure 5 shows the wiring system employed in the thermocouple circuits.

7. Rate of Heating Joly,[1] Dana,[2] Mellor,[3] Dittler,[4] and others have emphasized the importance of the time of heat treatment when one is investigating the thermal properties of silicates. In order to keep any error arising from the speed at which heat was applied to the test pieces constant, the rheostat was so manipulated as to permit the attainment of a temperature of 1050°C in about 55 minutes—a time sufficient for the necessary manipulations involved in making a determination. All samples were dried overnight at 65°C.

8. Advantages of Method (*a*) This method gives values for the interval specific heats which indicate the actual number of calories required to be added from some outside source (from the fuel) in order to raise the temperature of a given material from 0 to *t*°C taking into account any and all thermal processes which the material might undergo on being heated.

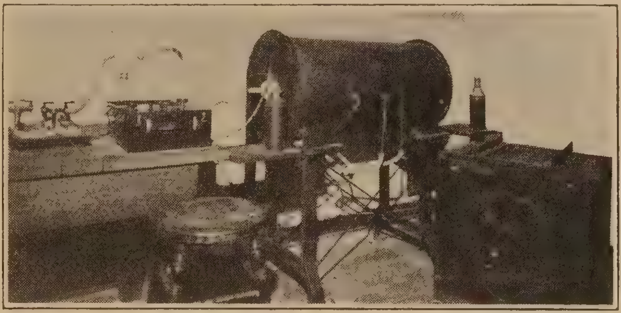

FIG. 6.

(*b*) It gives the exact temperatures at which the various thermal processes begin and end.

(*c*) It gives the actual quantitative figures for the various thermal processes.

(*d*) The apparatus is inexpensive and easy of manipulation.

The values obtained in this investigation and herewith presented are probably correct to within 10% of the absolute values.

Figure 6 shows a photograph of the apparatus used in this investigation.

Experimental Work

1. Standardization of Thermocouples The thermocouples were made of No. 22 gage chromel and alumel wire. They were standardized by noting the voltage generated by the couple when the one junction was at the temperature of melting ice and the other at the freezing temperature of metals of certified freezing points obtained from the U. S. Bureau of Standards. About

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[1] J. Joly, Brit. Assn. Report, 750 (1900).

[2] L. I. Dana, "Melting Point of Refractory Materials," *Amer. Inst. Min. Met. Eng.* (Pyrometry), 267–84 (1920).

[3] J. W. Mellor, Clay and Pottery Industries, 32, 247; 37, 309 (1914).

[4] E. Dittler, "Beitrage zur Thermochemie der Silikate," *Z.f. Anorg. Chem.*, **69**, 273–304 (1911).

50 cc. of each of the metals, tin, aluminum, zinc and copper, were used. The metal samples were placed in graphite crucibles of approximately 1 inch in internal diameter and 4 inches high. The samples were heated well beyond their melting temperatures in an Ajax-Northrup high frequency induction furnace, after which one junction of the couple being tested was inserted into the metal and voltage readings as a function of time taken. The thermocouple was protected from the metal bath by a thin-walled graphite tube. In order to avoid any possibility of oxidation of the metals, they were covered with pure graphite powder. The voltage decreases in a regular manner until the freezing temperature of the metal is reached after which the voltage remains constant (and likewise the temperature of the metal) until the end of the solidification process, when it again falls regularly. Figure 7 shows a typical curve obtained by plotting voltages against time. The break in the curve gives the voltage generated by the thermocouple at the freezing temperature of the metal in question. The voltages generated at the freezing temperatures of the various metals is as follows:

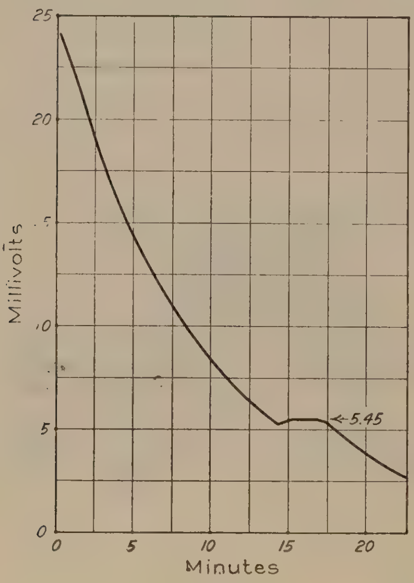

Fig. 7.

Metal	Millivolts	Temperature °C
Tin	9.7	231.9
Zinc	17.4	419.4
Aluminum	27.4	658.9
Copper	44.4	1083.0

Figure 8 shows the average standardization curve.

It is to be noted that this standardization of the thermocouples also served to standardize the Brown potentiometer, as it was used to record the millivolts generated.

2. Rose Quartz Of the materials which Cohn[1] worked with, that which could be obtained with greatest probability of an actual duplication was rose quartz. With the intention of comparing the values obtained by Cohn with those obtained by the method employed

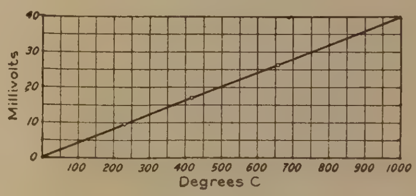

Fig. 8.

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[1] *Loc. cit.*

TABLE VI

CHEMICAL ANALYSIS OF THE MATERIALS INVESTIGATED

Total	North Carolina kaolin	Brandywine feldspar	Georgia kaolin	Delaware kaolin	Kentucky ball clay	Magnesia spinel	Florida kaolin	Disapore clay	Oil shale	Fire-brick body No.1	Fire-brick body No.2	Fire-brick body No.3	Fire-brick body No.4	Fire-brick body No.5
H_2O	16.83	.40	13.83	13.05	8.35		14.86	13–14	.31					
SiO_2	44.50	68.98	45.70	48.15	61.25	2.27	45.67	7–10	45.27	70.58	50.70	56.28	59.46	64.60
Al_2O_3	37.55	17.50	38.20	36.38	25.05	69.53	38.45	72–78	10.44	24.10	41.79	39.50	36.07	30.13
Fe_2O_3	.54	.17	.60	.90	1.30		.75	1.50	3.52	1.49	2.57	2.80	2.72	2.73
TiO_2	.03			.22	1.35		.10			3.05	2.68			1.52
MgO	trace	.10		trace	.20	28.20	.05	trace	7.38	.24	.53	.32	.48	.45
CaO	trace	.20		trace	.10		trace	.20	21.91	.09	.37	.42	.68	.44
K_2O	.75	10.00	.14	.81			.06							
Na_2O		3.05	.20											
MnO		.004			1.90									
R_2O_3 (principally Al_2O_3)										.55	1.10	1.10	.41	.63
Ash									.60					
Volatile matter and fixed carbon									38.72					

TABLE VII

SPECIFIC HEATS OVER THE INTERVAL 0–t°C

Rose Quartz		North Carolina kaolin		A-1 English china clay		Brandywine feldspar		Georgia kaolin		Delaware kaolin	
Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat
156.0°C	.194	107.1°C	.381	104.5°C	.369	108.5°C	.209	102.8°C	.380	105.7°C	.370
205.0	.201	155.8	.394	152.0	.382	157.7	.218	151.5	.391	153.4	.386
252.9	.208	203.6	.402	200.0	.393	206.0	.225	198.8	.402	203.6	.393
301.3	.214	251.0	.415	248.6	.406	253.4	.234	247.7	.414	253.4	.405
350.6	.221	299.4	.426	297.5	.417	301.8	.242	296.5	.424	302.7	.416
398.4	.227	347.7	.438	345.3	.427	350.1	.248	344.4	.435	350.1	.430
446.4	.233	396.5	.451	392.9	.438	398.4	.255	391.7	.448	396.5	.444
495.4	.236	445.0	.462	440.2	.449	446.5	.261	437.8	.458	442.6	.455
541.7	.242	494.0	.477	480.9	.465	496.0	.267	480.9	.472	484.8	.470
592.3	.246	540.2	.502	512.6	.487	542.2	.272	510.2	.498	515.5	.494
641.0	.249	590.3	.532	537.0	.517	591.2	.277	534.2	.529	537.6	.528
689.9	.251	639.0	.568	552.8	.553	639.0	.282	557.6	.557	567.8	.549
739.4	.254	687.0	.547	616.2	.538	687.5	.284	628.7	.536	628.3	.539
789.7	.256	736.0	.517	705.8	.508	737.6	.286	722.4	.505	713.1	.513
839.5	.257	785.3	.505	780.5	.493	787.8	.288	781.8	.500	778.5	.505
888.8	.257	834.2	.505	831.8	.493	838.6	.289	834.2	.500	831.7	.504
939.3	.258	883.0	.505	884.9	.493	889.3	.289	884.7	.501	883.0	.503
989.4	.260	931.5	.505	934.0	.493	940.8	.290	935.4	.501	933.4	.504
1039.7	.261	956.1	.509	961.0	.492	991.4	.292	962.2	.502	960.0	.504
		980.6	.483	1048.0	.465	1040.8	.293	1022.2	.488	1036.8	.483
		1004.8	.507	1013.2	.495			1013.1	.504	1013.6	.504
		1029.0	.512	1035.8	.499			1035.9	.507	1034.9	.510

TABLE VII (*continued*)

SPECIFIC HEATS OVER THE INTERVAL 0–t°C

Kentucky ball clay		Magnesia spinel		Florida kaolin		Disapore clay		Oil shale		Firebrick body No. 1	
Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat
109.0°C	.333	149.6°C	.201	109.5°C	.359	157.2°C	.333	107.1°C	.339	105.9°C	.324
158.2	.348	196.4	.207	159.1	.375	206.5	.343	163.0	.337	155.8	.334
206.9	.358	243.3	.214	207.9	.388	255.3	.355	251.4	.295	206.0	.341
255.9	.372	291.3	.220	257.2	.401	306.1	.364	495.8	.208	255.3	.352
307.6	.380	339.5	.225	307.1	.413	356.4	.372	544.4	.212	304.7	.367
360.2	.387	398.9	.229	356.9	.423	403.2	.385	617.2	.238	353.5	.373
405.1	.401	437.3	.234	402.8	.440	448.8	.396	675.7	.240	403.7	.382
449.8	.415	487.2	.237	448.4	.450	487.2	.413	1050.0	.285	453.8	.389
489.2	.431	534.4	.242	489.6	.467	498.0	.445			494.0	.403
516.0	.457	584.0	.246	515.1	.498	516.3	.485			521.3	.429
545.7	.481	632.2	.250	540.0	.528	577.4	.476			543.3	.458
605.1	.476	681.4	.252	561.6	.558	675.4	.443			608.4	.449
676.3	.463	731.6	.254	657.9	.517	738.9	.437			689.4	.429
736.0	.459	783.4	.255	736.0	.499	791.1	.438			744.4	.430
789.7	.461	834.2	.255	792.6	.498	841.5	.439			795.1	.431
840.5	.461	886.4	.255	844.0	.499	891.8	.440			845.5	.433
890.8	.462	939.3	.256	895.2	.499	941.7	.441			897.7	.433
941.3	.462	991.3	.257	945.6	.501	967.1	.442			946.7	.435
968.3	.463	1042.2	.257	971.7	.501	993.3	.446			990.3	.428
996.7	.466			1011.5	.497	1018.5	.444			997.3	.438
1018.5	.466			1019.5	.504	1043.7	.445			1044.7	.441
1042.7	.462			1044.9	.507						

TABLE VII (*concluded*)

SPECIFIC HEATS OVER THE INTERVAL 0–t°C

Firebrick body No. 2		Firebrick body No. 3		Firebrick body No. 4		Firebrick body No. 5	
Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat	Temp.	Specific heat
101.4°C	.331	102.3°C	.327	102.9°C	.324	99.5°C	.321
152.9	.333	155.8	.325	154.4	.329	154.6	.316
203.6	.338	206.0	.331	204.5	.332	206.0	.319
255.3	.344	256.8	.340	254.6	.343	256.8	.328
306.6	.352	306.6	.350	306.6	.350	309.0	.337
358.8	.360	356.3	.359	358.3	.357	359.0	.343
409.0	.368	405.2	.369	406.3	.368	411.7	.351
459.0	.376	452.2	.379	454.1	.378	465.8	.354
498.8	.390	496.9	.390	496.9	.391	496.9	.378
527.2	.414	525.7	.413	524.7	.414	524.2	.399
550.6	.442	546.7	.439	553.5	.435	550.6	.423
614.3	.434	604.5	.438	613.3	.432	610.6	.419
687.0	.423	674.9	.427	678.7	.424	688.4	.403
740.4	.423	741.3	.420	741.8	.418	742.3	.403
791.6	.425	794.1	.420	794.1	.420	796.5	.403
843.0	.425	845.9	.421	845.4	.421	847.4	.404
895.7	.425	896.2	.421	898.1	.421	898.1	.405
949.1	.425	951.0	.421	950.1	.421	966.7	.399
983.0	.422	986.5	.417	988.9	.415	977.1	.405
995.9	.431	999.2	.427	998.2	.426	1001.1	.411
1044.7	.431	1046.7	.428	1036.2	.426	1046.2	.413

in this investigation, the values for the interval specific heat of rose quartz were determined. The sample was obtained from near Custer, South Dakota, being kindly furnished by A. Brant of the Department of Mineralogy. Although the chemical analysis of this particular specimen was not available, E. F. Holden[1] gives the analysis of a typical rose quartz sample obtained from the Custer district to be as follows:

Loss on ignition	.17%	MnO	.0003%
Total solid impurities	.13	Li_2O	.003
Total impurities	.3	Fe_2O_3	.012

As heat is applied, the temperature of the sample rises quite uniformly, following the temperature of the quartz reference sample very closely. Therefore, this material undergoes no marked thermal changes. The calory-temperature curve indicates that slight exothermic processes take place at about 450°C and 850°C. Also, there appears to be a slight endothermic process beginning at about 550°C and extending over a range of about 200°.

Table VII shows the values obtained for the interval specific heat of rose quartz from 0 to t°C.

In Figure 10 is shown the number of calories required to heat one gram of rose quartz from 0 to t°C. Calories are calculated according to equation (1).

3. North Carolina Kaolin

The North Carolina kaolin was mined near Spruce Pine, Mitchell Co., N. C., and has the chemical analysis shown in Table VI.

It was found that 1.15 grams gave the maximum temperature effect and this was, therefore, the quantity used in the final determination. This was ascertained by keeping the weight of quartz constant and using various weights of the clay. Beginning with one gram, the temperature difference continually increased with increasing quantities of clay until 1.15 gram was employed, after which a further increase of clay gave no corresponding increase in temperature differences. In a similar manner it was found that 2.25 grams of quartz gave the maximum temperature effect and this quantity was, therefore, used in this and all other determinations.

An endothermic process begins at about 200°C and extends to about 675°C, reaching its maximum intensity at about 550°C. This endothermic process is due to the driving off of the water contained in the clay. Quantitatively, this reaction absorbs 150 calories per gram of air dried (65°C) clay. This value is obtained from the temperature-calory curve by projecting the curves in a straight line and measuring the calories directly along the central portion. The method of doing this is indicated by the dotted lines on Fig. 9. Such endothermic processes scarcely, if ever, present an exactly horizontal section of the curve and must, therefore, be extrapolated from the curve sections above and below the reaction in question.

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[1] E. F. Holden, "The Cause of Color in Rose Quartz," *Amer. Mim.*, **75** [9, 4] (1924).

An exothermic process appears at about 970°C, the chemical significance of which is not definitely known. The extent of this reaction is 40 calories per gram of air dried (65°C) clay. On the calory-temperature curve, the temperature rises fairly regularly with the inducted heat up to the temperature at which the exothermic process begins. Then appears a sudden rise in temperature of about 70°C, making the clay hotter than the furnace. The loss of heat from the sample then becomes quite large and the temperature falls until it reaches that of the furnace, when it again rises in a regular manner with the inducted heat. In this manner originates the sharp break in the calory-temperature curve. The intensity of the exothermic reaction is obtained by extrapolation of the middle portion of the upper curve section, from the point at which the sample begins to lose an appreciable amount of heat to the furnace, to the middle portion of the lower curve section. If there had been no loss of heat from the sample, the steady rise would have begun at 1041°C so the curve is projected from this temperature. This is illustrated by the dotted lines in Fig. 9.

For all temperatures above those at which exothermic processes occur, it is necessary to extrapolate the upper curve sections from the points at which the samples begin to lose an appreciable amount of heat to the furnace. This is illustrated by the dotted line in Figure 9. Thus, 543 (not 572 calories as read from the original calory-temperature curve) are required to heat one gram of air dried North Carolina kaolin from 0°C to 1100°C. Of course, some heat is lost to the furnace just as soon as the sample gets hotter than the furnace, as is evidenced by the slight upward trend of the curve after starting the exothermic process. However, this loss of heat is greatly overbalanced by the effect of the exothermic process until this process ceases—then appears the sharp break in the curve.

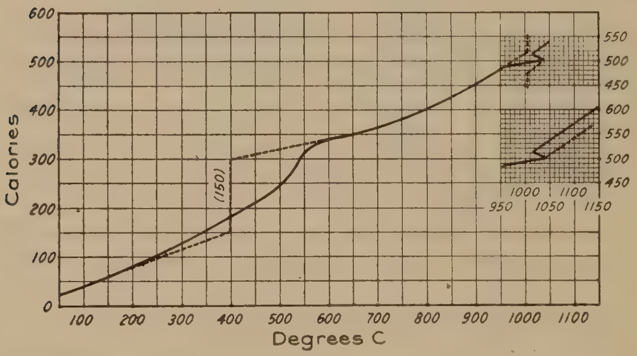

FIG. 9.—The exothermic reaction amounts to 40 calories per gram as read from the calory base line. The endothermic reaction is 150 calories per gram as read from the calory base line.

TABLE VIII

SHOWING THE NUMBER OF CALORIES REQUIRED TO HEAT ONE GRAM OF THE RESPECTIVE MATERIALS FROM 0–t°C

Temp.	A-1 English china clay	Georgia kaolin	Delaware kaolin	North Carolina kaolin	Florida kaolin	Kentucky ball clay	Diaspore clay	Oil shale	Magnesia spinel	Rose quartz	Feldspar	Firebrick body No.1	Firebrick body No.2	Firebrick body No.3	Firebrick body No.4	Firebrick body No.5
100°C	43	38	36	40	38	37	37	32	20	20	21	38	32	32	37	39
200	87	79	79	80	76	68	70	65	47	37	43	68	68	68	66	67
300	136	130	130	130	125	112	106	75	75	62	70	107	105	104	103	101
400	185	183	180	183	171	159	150	85	101	86	103	150	136	145	144	135
500	240	243	240	245	239	236	232	105	129	113	135	203	195	194	195	188
600	334	332	239	340	326	285	274	135	155	144	168	273	261	268	263	254
700	360	360	379	364	352	320	306	175	181	172	200	305	293	293	293	285
800	405	402	406	403	395	366	350	235	208	202	231	346	340	337	336	325
900	454	451	455	453	450	416	400	270	235	223	262	390	382	379	379	365
1000	487	496	495	496	500	465	450	320	262	157	295	426	419	415	415	401
1100	525	554	545	543	565	507	500	365	290	295	334	475	473	461	462	450
1200												525	526	507	506	497
1300												573	580	555	553	550

4. A-1 English China Clay This material was kindly furnished by Hammill and Gillispie, Inc., and acknowledgment is here gratefully made.

An endothermic process begins at about 250°C and extends to about 725°C, reaching its maximum intensity at about 550°C. This reaction absorbs 123 calories per gram of air dried (65°C) clay.

At a temperature of about 970°C, the calory-temperature curve shows the same sharp break as indicated for North Carolina kaolin, being due to the exothermic reaction taking place. This exothermic process evolves 35 calories per gram of air dried (65°C) clay.

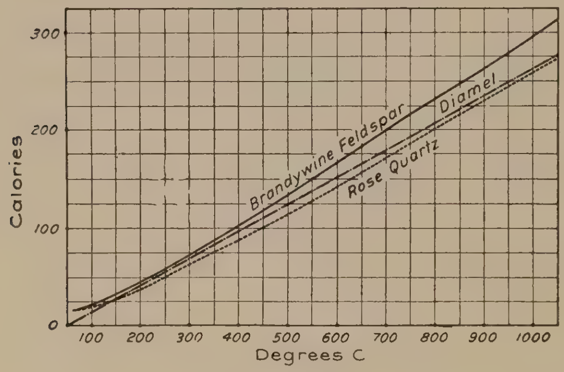

Fig. 10.

The consumption of heat up to any given temperature, the value of vital concern to the industry can be obtained by referring to Fig. 11, in which calories are plotted against temperature. The values for the interval specific heats of A-1 English china clay from 0 to *t*°C are shown in Table VII.

5. Feldspar The feldspar used in this investigation is that known as "Brandywine" feldspar. It was mined near Brandywine Summit, Pa., and has the chemical composition shown in Table VI.

The temperature of the feldspar rose uniformly throughout the heating process, showing that feldspar undergoes very little, if any, thermal processes. The values obtained for the interval specific heat of Brandywine feldspar from 0 to *t*°C are shown in Table VII.

6. Georgia Kaolin This material was mined near Dry Branch, Ga., and has the chemical composition shown in Table VI.

An endothermic process begins at about 250°C and extends to about 650°C, reaching its maximum intensity at about 550°C. This reaction absorbs 127.5 calories per gram of air dried (65°C) clay.

At a temperature of about 980°C appears the same exothermic reaction as was observed in the case of North Carolina kaolin and A-1 English china clay. This reaction evolves 22.5 calories per gram of air dried (65°C) clay.

As a general statement, one can say that the behavior of primary and secondary kaolin on firing is practically the same. That is, both show a marked endothermic reaction in the neighborhood of 600°C, being due to the expulsion of chemically bound water, and a sharp exothermic reaction at about 975°C, the chemical significance of which is not definitely known. Either requires an average of about .5 calories per gram per degree in order to raise its temperature from 0 to *t*°C.

Table VII shows the interval specific heats of Georgia kaolin from 0° to *t*°C.

7. Delaware Kaolin This material was mined near Hockessen, Del., fires to a light salmon color, and has the chemical composition shown in Table VI.

As in the case of the other kaolins, an endothermic reaction at about 600°C and an exothermic reaction at about 970°C are evident. The endothermal process begins at about 250°C and extends to about 650°C, reaching its maximum intensity at about 550°C. This reaction absorbs 118 calories per gram of air dried (65°C) clay. The exothermic reaction begins at about 975°C and evolves 32 calories per gram of air dried (65°C) clay.

Table VII shows the values for the interval specific heats of Delaware kaolin over the range 0 to *t*°C.

8. Kentucky Ball Clay This material was mined near Mayfield, Ky., and has the chemical composition shown in Table VI.

Qualitatively, this material shows the same general behavior on heating as the kaolins. However, the intensity of both the endothermic and exothermic reactions is decidedly less pronounced. In fact, the exothermic reaction in the neighborhood of 980°C was so insignificant that it caused no sharp break in the calory-temperature curve, Fig. 12. The endothermal process began at about 250°C and extended to about 680°C, reaching its maximum at about 540°C. This reaction absorbs 90 calories per gram of the air dried (65°C) material.

The exothermic reaction which begins at about 980°C evolves 5 calories per gram of the air dried (65°C) clay.

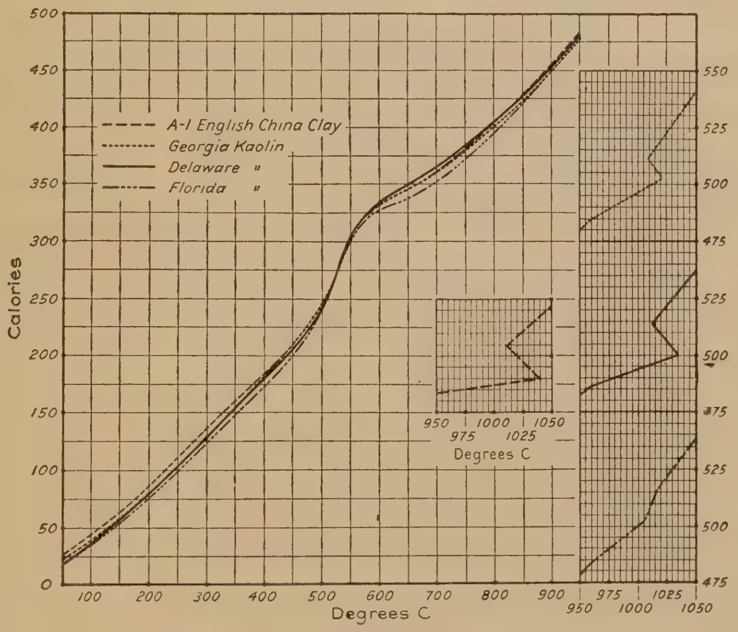

FIG. 11.

The values for the interval specific heat from 0° to *t*°C are shown in Table VII.

9. Magnesia Spinel

As a representative of the spinel groups, the values for the interval specific heats of an artificial spinel (diamel) were determined. An analyzed sample of this material was kindly placed at the author's disposal by H. Fisk, Research Fellow of the U. S. Bureau of Mines. This particular sample has the chemical composition shown in Table VI.

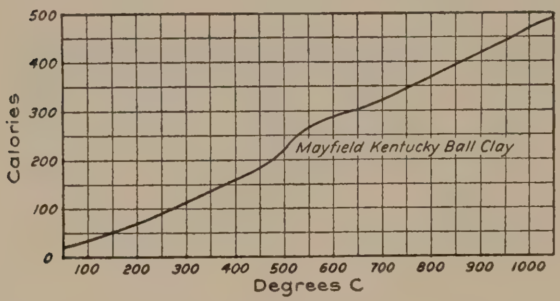

FIG. 12.

The temperature calory curve, Figure 10, is a perfectly straight line, showing that this material undergoes no thermal changes on being heated to about 1050°C.

The values for the interval specific heats of magnesia spinel over the interval 0 to t°C are shown in Table VII.

10. Florida Kaolin

This material was mined near Edgar, Putnam Co., Florida, and has the chemical composition shown in Table VI.

As in the case of the other kaolins, an endothermic reaction at about 970°C is very much in evidence. The endothermal process begins at about 250°C and extends to about 675°C, reaching its maximum at about 550°C. This reaction absorbs 122.5 calories per gram of air dried (65°C) clay.

The exothermic reaction begins at 980°C and evolves 10 calories per gram of air dried clay.

The values for the interval specific heats of Florida kaolin over the interval 0 to t°C are shown in Table VII.

11. Diaspore Clay

As a typical representative of the diaspore type of clay, a Missouri diaspore clay was selected. This material was kindly placed at the author's disposal by the General Refractories Co., Philadelphia, Pa. It has the chemical composition shown in Table VI.

As in the case of the kaolins, an endothermic reaction took place at about 550°C. However, there was no exothermic reaction at 970°C. The endothermic reaction reaches its maximum intensity at about 520°C. It absorbs 100 calories per gram of air dried (65°C) material.

The values for the interval specific heats of Missouri diaspore clay from 0 to t°C are shown in Table VII.

12. Oil Shale

As a representative of a class of material which contains a large amount of carbonaceous matter, oil shale was selected. This material was obtained from the Oil Shale

Laboratory, U. S. Bureau of Mines, Boulder, Colorado. It has the chemical composition shown in Table VI.

An exothermic reaction starts at about 160°C and extends to about 675°C. Any water that is in the shale is being driven off over this period and is absorbing heat. Also, there is bound to be more or less distillation of the volatile matter and of course heat is absorbed in this process. On the other hand, the volatile matter is ignited by the heat of the furnace and burns quite vigorously, thereby evolving heat. The sum total of the endothermic and exothermic reactions is 150 calories evolved per gram of air dried (65°C) material. After this violent exothermic process, the shale rises uniformly in temperature as heat is added until it reaches about 750°C, when another exothermic process begins and extends to about 950°C. This reaction is due, in all probability, to the burning out of the fixed carbon and amounts to 34 calories per gram of the air dried (65°C) shale.

The shale sample at the peak of the first exothermic process was almost 300°C hotter than the reference material and, of course, rapidly lost heat by radiation to the furnace and by conduction down the thermocouple leads. This was, of course, of such a nature that the sample soon cooled to near the furnace temperature after the exothermic process was completed; thus, the effect of the evolved heat on the specific heat values was lost. If the material were in a system such as to prevent the loss of this excess heat, the value of the exothermic processes would have to be subtracted from the calory-temperature curve (Fig. 13), in order to find the number of calories required to heat it to any given temperature. That is, the upper curve section should be projected from the point *B*.

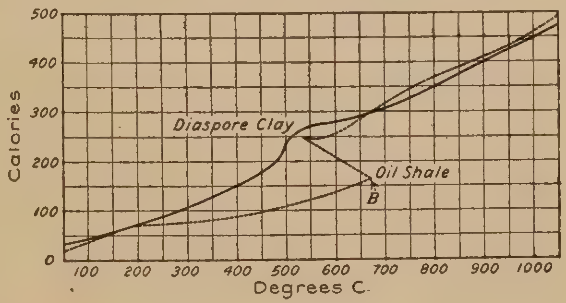

FIG. 13.

The oxidation was so severe that a thermocouple never survived over a single heat.

The values for the interval specific heats of Colorado oil shale over the interval 0 to *t*°C are shown in Table VII.

13. Firebrick Body No. 3 This material was kindly placed at the author's disposal by the Ashland Fire Brick Co., Haywood, Ky. It is representative of a high grade fire brick manufactured from Kentucky clays. It has the chemical composition shown in Table VI.

Qualitatively, this material showed the same behavior on heating as did the kaolins, exhibiting an endothermic reaction in the neighborhood of 500°C and an exothermic reaction at about 956°C. However, the reactions were much less intense. The thermal behavior of this material on heating more nearly approximates that of ball clay than that of kaolin. The endothermal process, beginning at 300°C and extending to 600°C, absorbs 62 calories per gram of air dried (65°C) material. The exothermal process which takes place at about 956°C evolves 6 calories per gram of air dried (65°C) material.

The values for the interval specific heats of this firebrick body over the interval 0 to *t*° are shown in Table VII.

It is to be recalled that this firebrick body (as were the four following firebrick bodies) was one of those investigated by the Ceramic Experiment Station of the U. S. Bureau of Mines in the investigation of the distribution of heat in refractory kilns.[1] This material is similar to that used in Tests A and B, Test Serial Numbers 5 and 6, Table I. Referring to Table I, one sees that 16.6 and 23.6% of the total heat in the fuel was used, respectively, to heat the brick in Tests A and B to their finishing temperature. These values were calculated from specific heat values of 0.264 for Test A and 0.265 for Test B. This gives an unaccounted for loss of 23.4 and 22.8% of the total heat available in the fuel used in Tests A and B respectively. The initial and finishing temperature in Test A was 33°C and 1192°C respectively. The initial and finishing temperature in Test B was 24°C and 1209°C respectively.

By extrapolating the curve in Fig. 14 to 1209°C it is evident that 509 calories and 517 calories are required to heat one gram of this material from 0°C to the finishing temperature, 1192°C and 1209°C respectively, in Tests A and B. On subtracting 10.8 (which is the number of calories required to heat one gram of this material from 0°C to 33°C, the initial temperature in Test A) from 509 and 7.8 (which is the number of calories required to heat one gram of this material from 0°C to 24°C, the initial temperature in Test B) from 517, it is evident that 498.2 calories and 509.2 calories are respectively required to heat this firebrick body over the temperature intervals employed in Tests A and B. This gives 0.432 and 0.430 as the specific heat of this material over the temperature interval employed in Tests A and B respectively. From these interval specific heats, it is calculated that 27.2% and 38.3% of the available heat in the fuel was used to actually heat the brick in Tests A and B respectively. This gives an unaccounted for loss of heat of 13 instead of 23.4 in Test A and 8.2 instead of 22.8 in Test B.

Thus, it is apparent that our ceramic kilns are considerably more efficient users of fuel than we have ordinarily supposed them to be. Also, it is apparent that the method of mixtures gives interval specific heat values which are entirely too low for a large portion of ceramic materials and bodies.

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[1] *Loc. cit.*

14. Firebrick Body No. 5 This material was kindly placed at the author's disposal by the Chicago Retort and Fire Brick Co., Ottawa, Ill. It is representative of the stiff-mud brick made in that district. It has the chemical composition shown in Table VI.

This material undergoes an endothermic reaction which begins at about 340°C, reaching its maximum intensity at 550°C. This endothermal process absorbs 65 calories per gram of air dried (65°C) material. An exothermic reaction takes place at about 931°C which evolves 10 calories per gram of air dried (65°)C material.

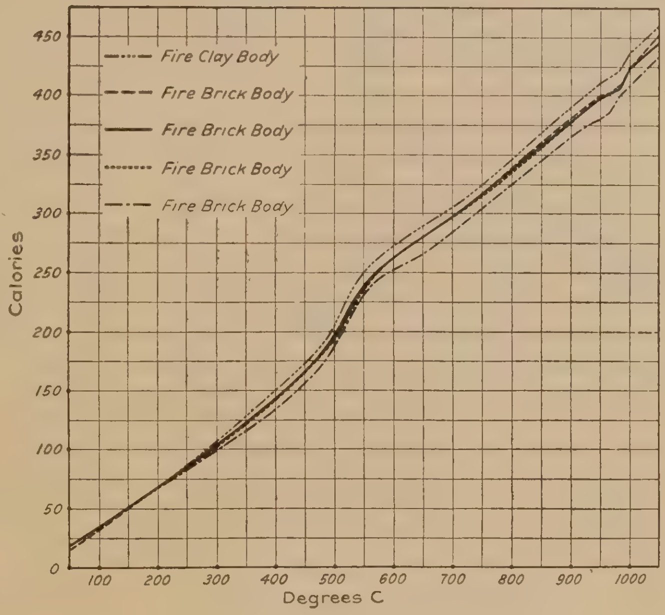

FIG. 14.

The values for the interval specific heats of this firebrick body over the interval 0 to *t*°C are shown in Table VII.

This material is similar to that used in Tests A and B, Test Serial Numbers 9 and 10, Table I. Referring to Table I, one sees that 23.8 and 22.0% of the total heat in the fuel was used, respectively, to heat the brick in Tests A and B to their finishing temperature. These values were calculated from specific heat values of .264 for Test A and .262 for Test B. This gives an unaccounted for loss of 18.7 and 29.6% of the total heat available in the fuel used in Tests A and B respectively. The initial and finishing temperature in Test B was 33 and 1148°C respectively.

By extrapolation of the curve in Fig. 14 according to the procedure outlined for firebrick body No. 3, it was found that 37.5 and 34.8% of the total heat available in the coal was really used to heat the brick in Tests A and B to their respective finishing temperatures. This gives an unaccounted for loss of heat of 5.2 instead of 18.7 in Test A and 17.0 instead of 29.6 in Test B. The large unaccounted for heat loss in Test B is due to lack of proper temperature measurements in the bottom of the kiln.

15. Firebrick Body No. 4 This material was kindly placed at the author's disposal by the Charles Taylor and Sons Co., McCall, Ky. It has the chemical composition shown in Table VI.

This material undergoes an endothermic reaction which begins at about 300°C and extends to about 585°C, reaching its maximum intensity at 553°C. This endothermal process absorbs 60 calories per gram of air dried (65°C) material. An exothermic reaction takes place at about 956°C which evolves 8 calories per gram of air dried (65°C) material.

The values for the interval specific heats of this firebrick body over the interval 0 to *t*°C are shown in Table VII.

This material is similar to that used in Tests A and B, Test Serial Numbers 7 and 8, Table I. Referring to Table I, one sees that 26.3 and 27.7% of the total heat in the fuel was used, respectively, to heat the brick in Tests A and B to their finishing temperatures. These values were calculated from specific heat values of 0.263 for Test A and 0.266 for Test B. This gives an unaccounted for loss of 12.6 and 13.6% of the total heat available in the fuel used in Tests A and B respectively. The initial and finishing temperatures in Tests A and B were 29°C and 1152°C, and 24°C and 1213°C respectively.

By extrapolation of the curve in Fig. 14 according to the procedure outlined for firebrick body No. 3, it was found that 42.8 and 44.5% of the total heat available in the fuel was really used to heat the brick in Tests A and B to their respective finishing temperatures. This gives an unaccounted for loss of heat of −3.5 instead of 12.6 in Test A and of −3.3 instead of 13.2 in Test B.

16. Firebrick Body No. 1 This material was kindly placed at the author's disposal by the Brooklyn Fire Brick Works, Brooklyn, N. Y. It is representative of a New Jersey fireclay brick containing a high percentage of grog. It has the chemical composition shown in Table VI.

This material undergoes an endothermic reaction which begins at about 250°C, reaching its maximum intensity at 543°C. This endothermal process absorbs 67.5 calories per gram of air dried (65°C) material. An exothermic reaction takes place at about 956°C which evolves 9.5 calories per gram of air dried (65°C) material.

The values for the interval specific heats of this firebrick body over the interval 0 to *t*°C are shown in Table VII.

This material is similar to that used in Tests A and B, Test Serial Numbers 1 and 2, Table I. Referring to Table I, one sees that 19.4 and 15.7% of the total heat in the fuel was used, respectively, to heat the brick in Tests A and B to their finishing temperature. The values were calculated from specific heat values of .263 for Test A and .259 for

Test B. This gives an unaccounted for loss of 8.0 and 14.8% of the total heat available in the fuel used in Tests A and B respectively. The initial and finishing temperature in Test A was 16°C and 1172°C respectively. The initial and finishing temperature in Test B was 24°C and 1080°C respectively.

By extrapolation of the curve in Fig. 14, according to the procedure outlined for firebrick body No. 3, it was found that 32.1 and 26.4% of the total heat available in the fuel was really used to heat the brick in Tests A and B to their respective finishing temperatures. This gives an unaccounted for loss of heat of −4.7 instead of 8.0 in Test A and 4.3 instead of 14.8 in Test B.

17. Firebrick Body No. 2 This material was kindly placed at the author's disposal by the Kier Fire Brick Co., Salina, Pa. It is representative of the best of the Clarion flint fireclay brick. It has the chemical composition shown in Table VI.

This material undergoes an endothermic reaction which begins at about 360°C and extends to about 600°C, reaching its maximum intensity at 550°C. This endothermal process absorbs 55 calories per gram of air dried (65°C) material. An exothermic reaction takes place at about 956°C which evolves 9.5 calories per gram of air dried (65°C) material.

The values for the interval specific heats of this firebrick body over the interval 0 to *t*°C are shown in Table VII.

This material is similar to that used in Tests A and B, Test Serial Numbers 3 and 4, Table I. Referring to Table I, one sees that 16.5 and 17.3% of the total heat in the fuel was used, respectively, to heat the brick in Tests A and B to their finishing temperatures. The values were calculated from specific heat values of .262 for Test A and .266 for Test B. This gives an unaccounted for loss of 10.6 and 16.2% of the total heat available in the fuel used in Tests A and B respectively. The initial and finishing temperature in Test A was 20°C and 1168°C respectively. The initial and finishing temperature in Test B was 29°C and 1218°C respectively.

By extrapolation of the curve in Fig. 14, according to the procedure outlined for firebrick body No. 3, it was found that 27.6 and 28.9% of the total heat available in the fuel was really used to heat the brick in Tests A and B to their respective finishing temperatures. This gives an unaccounted for loss of heat of −.3% instead of 10.6% in Test A and of 4.9% instead of 16.2% in Test B.

Further Investigations

Since knowledge of the specific heats of ceramic bodies greatly facilitates the ease with which firing efficiency, various types of kilns, and methods of firing can be compared as well as presenting the data absolutely essential for heat balances where all factors are measured (as is strikingly illustrated in the case of the U. S. Bureau of Mines investigation into the distribution of heat in refractory kilns), it seems desirable to have the interval specific heats of as many ceramic materials and bodies determined as is practicable. From a scientific standpoint, it is desirable to have the interval specific heats of almost every known material. Therefore, the substances available for specific heat determinations and whose values are desired is practically unlimited.

The determinations made in this investigation extend over the range 0° to about 1050°C. It would be highly desirable if future determinations could be carried up to as high as 1500°C or thereabouts. It is highly desirable that future investigators determine the interval specific heats and thermal processes not only for single materials but also for mixtures, including all types of ceramic bodies. At higher temperatures the thermal processes will, undoubtedly, be quite complex and intensely interesting, especially in case of the bodies.

The determining of the actual quantitative figures for the various thermal processes which a material or body undergoes on heating is a distinct scientific achievement and it is to be hoped that further work along this line will be carried out in the near future. If such investigations are carried out, it would present a much more comprehensive insight into the behavior of a substance undergoing heating if the temperature measurements were made every 5°C instead of about every 50°C as was done in the present investigation.

Conclusions

In the way of general conclusions, the following might be said:

1. All kaolins undergo an endothermic process in the neighborhood of 575°C which amounts to about 100 calories per gram of clay.
2. All kaolins undergo an exothermic process in the neighborhood of 960°C which amounts to about 25 calories per gram of clay.
3. It requires about 500 calories to heat one gram of any kaolin from 0 to 1000°C, the specific heat over this interval being about 0.5.
4. All firebrick bodies undergo an endothermic process in the neighborhood of 550°C which amounts to about 55 calories per gram of body.
5. All firebrick bodies undergo an exothermic process in the neighborhood of 950°C which amounts to about 9 calories per gram of body.
6. It requires about 510 calories to heat one gram of any firebrick body from 25–1200°C, the specific heat over this interval being about 0.433. The actual amount of heat will, of course, depend upon the

amount of grog present, the larger the amount of grog the less the heat required.

7. Ball clays undergo an endothermic reaction in the neighborhood of about 550°C which amounts to about 90 calories per gram of clay.

8. Ball clays undergo a slight exothermic reaction in the neighborhood of 975°C which amounts to about 5 calories per gram of clay.

9. It requires about 450 calories to heat one gram of ball clay from 0°–1000°C, the specific heat over this interval being about .45.

10. Diaspore clays undergo an endothermic process in the neighborhood of 525°C which amounts to about 100 calories per gram of clay.

11. Diaspore clays undergo no exothermic process up to 1050°C.

12. It requires about 450 calories to heat one gram of diaspore clay from 0°–1000°C, the specific heat over this interval being about 0.45.

In the way of specific conclusions, the following might be said:

1. About 487.5 calories are required to heat one gram of air dried (65°C) A-1 English china clay from 0°–1048°C, the specific heat over this interval being 0.465. This clay undergoes an endothermic reaction at about 550°C and an exothermic reaction at 970°C which amount to 123 and 35 calories, respectively, per gram of air dried material.

2. About 505.4 calories are required to heat one gram of air dried (65°C) North Carolina kaolin from 0–1046.5°C, the specific heat over this interval being 0.483. This clay undergoes an endothermic reaction at about 550°C and an exothermic reaction at 970°C which amount to 150 and 40 calories, respectively, per gram of air dried material.

3. About 500.7 calories are required to heat one gram of air dried (65°C) Delaware kaolin from 0–1036.8°C the specific heat over this interval being 0.483. This clay undergoes an endothermic reaction at about 550°C and an exothermic reaction at 975°C which amount to 118 and 32 calories, respectively, per gram of air dried material.

4. 500 calories are required to heat one gram of air dried (65°C) Georgia kaolin from 0–1022.2°C, the specific heat over this interval being 0.488. This clay undergoes an endothermic reaction at about 550°C and an exothermic reaction at 980°C which amount to 127.5 and 22.5 calories, respectively, per gram of air dried material.

5. About 530.2 calories are required to heat one gram of Florida kaolin, air dried at 65°C, from 0–1044.9°C, the specific heat over this interval being .507. This clay undergoes an endothermic reaction at about 550°C and an exothermic reaction at 980°C which amount to 122.5 and 10 calories, respectively, per gram of air dried material.

6. About 480.0 calories are required to heat one gram of Kentucky ball clay, air dried at 65°C, from 0–1042.7°C, the specific heat over this interval being .462. This clay undergoes an endothermic reaction

at about 540°C and an exothermic reaction at 980°C which amount to 90 and 5 calories, respectively, per gram of air dried material.

7. About 271.7 calories are required to heat one gram of air dried (65°C) rose quartz from 0–1039.7°C, the specific heat over this interval being 0.261.

8. About 305.0 calories are required to heat one gram of air dried (65°C) feldspar from 0–1040.8°C, the specific heat over this interval being 0.293.

9. About 268.2 calories are required to heat one gram of air dried (65°C) magnesia spinel from 0–1042.2°C, the specific heat over this interval being 0.257.

10. About 465.0 calories are required to heat one gram of air dried (65°C) Missouri diaspore clay from 0–1043.7°C, the specific heat over this interval being 0.445. This clay undergoes an endothermic reaction at about 550°C which amounts to 100 calories per gram of air dried material.

11. It requires about 300 calories to heat one gram of air dried (65°C) Colorado oil shale from 0–1050°C, the specific heat over this interval being about 0.285. This clay undergoes an exothermic reaction at about 300°C and an exothermic reaction at about 800°C amounting to 150 and 34 calories, respectively, per gram of air dried material.

12. About 441 calories are required to heat one gram of the air dried (65°C) firebrick body No. 3 from 0–1050°C, the specific heat over this interval being 0.420. This body undergoes an endothermic reaction at about 550°C and an exothermic reaction at 956°C which amount to 62 and 6 calories, respectively, per gram of air dried material.

13. About 430 calories are required to heat one gram of air dried (65°C) firebrick body No. 5 from 0–1050°C, the specific heat over this interval being .409. This body undergoes an endothermic reaction at about 550°C and an exothermic reaction at 932°C which amount to 65 and 10 calories, respectively, per gram of air dried material.

14. About 440 calories are required to heat one gram of the air dried (65°C) firebrick body No. 4 from 0–1050°C, the specific heat over this interval being .418. This body undergoes an endothermic reaction at about 550°C and an exothermic reaction at 957°C which amount to 60 and 8 calories, respectively, per gram of air dried material.

15. About 450 calories are required to heat one gram of air dried (65°C) firebrick body No. 1 from 0–1050°C, the specific heat over this interval being 0.428. This body undergoes an endothermic reaction at about 550°C and an exothermic reaction at 956°C which amount to 67.5 and 9.5 calories, respectively, per gram of air dried material.

16. About 443 calories are required to heat one gram of the air dried (65°C) firebrick body No. 2 from 0–1050°C, the specific heat

over this interval being 0.423. This body undergoes an endothermic reaction at about 550°C and an exothermic reaction at 956°C which amount to 55 and 7 calories, respectively, per gram of air dried material.

In closing the author wishes to express his gratitude to Arthur S. Watts, Head of the Department of Ceramic Engineering, Ohio State University, and G. A. Bole, Superintendent of the Ceramic Experiment Station, U. S. Bureau of Mines, under whose joint direction the work was carried out, for their many helpful suggestions and untiring interest in the work and problems that arose during the course of the investigation.

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ORIGINAL PAPERS

A STUDY OF MULLITE REFRACTORIES FORMED BY CALCINING CYANITE, THEIR INDUSTRIAL APPLICATION[1]

BY M. L. FREED[2]

ABSTRACT

This paper is a progress report of an investigation dealing with refractory bodies made of cyanite, either raw or calcined, and which was taken from a recently discovered deposit in India. The bodies were subjected to standard and modified laboratory tests for high grade refractories. Petrographic analyses indicated complete conversion to mullite in the test specimens and the results of the laboratory test indicate the bodies to be equal in quality to many so-called "super-refractories" now on the market.

Introduction

Review of Literature Cyanite, one of the sillimanite group of minerals, the other two being andalusite and sillimanite, has occupied the attention of numerous investigators for over a century. Recently Greig[3] ably summarized the progress of knowledge of the sillimanite group. A résumé of his summary follows:

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[1] Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce. Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Atlanta, Ga., Feb., 1926. (Refractories Division).

[2] M. L. Freed, Research Associate for Henry A. Golwynne.

[3] J. W. Greig, "Formation of Mullite from Cyanite, Andalusite and Sillimanite," *Jour. Amer. Ceram. Soc.*, **8**, 465 (1925).

Historical Summary

Saussure[1] first began to experiment with cyanite in 1785, noting that on calcination, the mineral becomes opaque white, develops an open structure and crumbles easily. In 1889–90 Saussure was confirmed by Vernadsky[2] in observations as to color and texture. Beekman[3] in 1902 obtained results agreeing with Vernadsky's, but concluded that the calcined product was not sillimanite as assumed by the former investigator. Shepherd, Rankin, and Wright[4] in 1909, however, obtained results agreeing with Vernadsky's and called the calcined product sillimanite, basing their findings on Vernadsky's density determination.

In 1924, Bowen and Greig[5] proved that calcining cyanite or any of the members of the sillimanite group of minerals, produced the compound $3Al_2O_3 \cdot 2SiO_2$ which they named mullite. In the same year Peck[6] described briefly the changes produced by calcining andalusite and cyanite, finding that cyanite breaks down to a chalky, friable mass, due to excessive expansion at the inversion point.

Greig[7] in his recent investigation found that the expansion during the alteration of cyanite into mullite (plus silica) is so great that any ware made largely from this material would be shattered on firing.

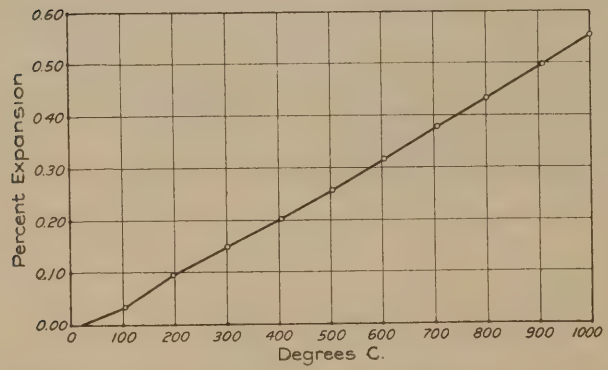

FIG. 1.—Thermal expansion of calcined cyanite (mullite and siliceous glass).

Scope of Investigation

Results of previous experimental work on cyanite have not been applied practically, no doubt because no commercially available deposit of pure cyanite was known to exist. The recent discovery in India of commercially available deposits containing over 95% pure cyanite prompted the continuation, on a semi-commercial scale, of the work of the many investigators mentioned.

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[1] Saussure, "Voyage dans les Alpes," **4,** Neuch., 845 (1796).

[2] Vernadsky, "Note sur l'influence de la haute temperature sur le disthene," *Bull. Soc. Fran. Min.*, **12,** 447 (1889). Also Vernadsky, "Sur la reproduction de la sillimanite," *Bull. Soc. Fran. Min.*, **13,** 257 (1890).

[3] E. H. Beekman, "Over't gedrag van distheen en sillimanite op hooge temperaturen," *Verslagen Wisen Natuurk. Afd. Kon. Akademie van Wetenschappen Amsterdam*, **11,** 295 (1902).

[4] E. S. Shepherd, G. A. Rankin and F. E. Wright, "The Binary Systems of Alumina with Silica, Lime and Magnesia," *Amer. Jour. Sci.*, **28,** 293 (1909).

[5] N. L. Bowen, J. W. Greig and E. G. Zies, "Mullite, A Silicate of Alumina," *Jour. Wash. Acad. Sci.*, **14,** 183 (1924).

[6] A. B. Peck, "Note on Andalusite from California; A New Use and Some Thermal Properties," *Amer. Mineralogist*, **9,** 123 (1924). "Changes in the Constitution and Microstructure of Andalusite, Cyanite and Sillimanite at High Temperatures and Their Significance in Industrial Practice," *Jour. Amer. Ceram. Soc.*, **8,** 407 (1925).

[7] J. W. Greig, *op. cit.*

Methods have been developed for converting cyanite into mullite by calcination, and for making refractories from mullite, either pure or mixed with bonding clay.

Mineralogy

Occurrence This deposit of Indian cyanite occurs as a compact and coarsely crystalline schist. Outcrops on the surface appear as huge boulders. The color of the mass in general varies from a grayish white to a somewhat reddish brown with an abundance of large blue crystals. Mining at present is done by the open quarry method.

Petrographic Composition A microscopic examination of thin sections and rock fragments of 75 different samples from widely separated parts of the deposit shows the occurrence to be mainly cyanite with small amounts of topaz, pyrophyllite, corundum as inclusions, and interstitial quartz.

Chemical Compositions Usual methods of analysis for the determinations of SiO_2, Al_2O_3, Fe_2O_3 and TiO_2 and loss on ignition were employed. Other constituent oxides were not determined.

A typical chemical analysis shows the recalculated Al_2SiO_5 to be over 90% for the regular run-of-mine and over 98% for hand-selected specimens. Table I shows the data obtained. Samples 1 (weathered rock) and 2 (unweathered) were selected from a trial shipment of 8 tons and samples 3 and 4 were specially picked samples containing an abundance of blue crystals.

TABLE I

RESULTS OF CHEMICAL ANALYSIS

	1	2	3	4
SiO_2	30.28	34.66	36.15	36.47
Al_2O_3	66.47	60.84	63.41	62.33
Fe_2O_3	.04	.07	—	—
TiO_2	1.49	1.18	—	—
Loss on ignition	1.02	.90	—	—
Undetermined, including alkali	.70	2.35	—	—

Preparation of Material

The crude rock was prepared for calcination by crushing to pieces approximately 3 to 5 inches in diameter and was then fired to 1450°C in a gas-fired laboratory kiln of the recuperative, semi-muffle type. It was found by petrographic examination that by this treatment even such large pieces were wholly converted to interlocking mullite crystals and a siliceous glass. Contrary to the findings of previous investigators, the calcining of the cyanite did not produce a friable, fragile mass. The larger fragments showed great expansion, but did not shatter (although a few deep cracks developed along the cleavage planes), and they could not be crumbled between the fingers. However, one sample of rock showed the presence of considerable quartz and did break up, when calcined, into a friable mass of free silica and dense pieces of mullite.

The prepared mullite was then crushed, ground, screened, and graded into various grain sizes from ¼ inch down to fines. The fines were produced by grinding 20-mesh material in a ball mill until all would pass a No. 200 sieve.

Preparation of Specimens

A series of bricks, 10x4½x2½ inches, was made by the dry-press process, using either pure cyanite, pure mullite, various mixtures of cyanite with clay, or mullite with clay. The pressed brick were dried and fired at 1500°C for three hours (cone 19). The compositions will be found in Table II.

TABLE II

COMPOSITIONS OF TRIAL BRICKS

Series	Cyanite %	Mullite %	Ball clay %	Fire clay %	Al_2O_3 %
A	100	—	—	—	—
B	—	100	—	—	—
C	45	—	—	55	—
D–K	—	75	25	—	—
D	—	80	20	—	—
D–F	—	75	—	25	—
E	61	—	—	10	29
F	—	61	10	—	29
G	75	—	—	25	—

The various sizes of material used (whether raw or calcined) were carefully proportioned and these proportions were the same for all compositions. When using pure cyanite or pure mullite, a solution of gum was used as a binder.

TABLE III

RESULTS OF FIRING TRIAL BRICKS

Series	% linear change after firing to cone 19		Description of brick
	Length	Width	
A	+ 3.75	+ 5.55	Sound
B	− 0.62	0.0	Excellent
C	+ 7.50	+ 5.55	Discolored
D	− 0.62	0.0	Excellent
D–K	0.0	0.0	Excellent
D–F	− 0.31	0.0	Excellent
E	+12.50	+11.11	Shattered, fragile
F	− 0.62	0.0	Excellent
G	+ 3.75	+ 2.77	Sound

Method of Testing and Results

Sound bricks were obtained in all the series (see Table III) with the exception of E (alumina, cyanite, and fire clay). These showed excessive expansion, were friable, and readily crumbled when touched. Series B (pure mullite); series D, D–K and D–F (mullite bonded with various clays); and series F (mullite, alumina and ball clay) all showed a maximum contraction of 0.62% in length and no change in width. The bricks all had a sound metallic ring when struck. Bricks of Series C were badly discolored by the fire clay. Bricks of Series A (pure cyanite) showed uniform expansion in all directions. The bricks of Series G (cyanite bonded with 25% fire clay) also exhibited uniform expansion and had the characteristic metallic ring of well-fired refractories.

Bricks of Series C were omitted in all the tests following because the bodies were badly discolored and expanded, due evidently to the high percentage of fire clay. Bricks of Series E were omitted because of the excessive expansion and poor mechanical strength. Bricks of Series D were omitted in the softening point determination and the quenching test because of the almost identical composition with series D–K. The effects of varying the amounts of clay bond with cyanite or mullite and the composition of bricks of series E (alumina, cyanite and fire clay) are to be made the object of a future study.

The softening point of bricks of series G was not determined because, after firing, they were identical with bricks of series D–F with respect to ultimate composition.

Load Test The specimen bricks were subjected to the standard load test following the method of the A.S.T.M. for "High Heat Duty Refractories" (Serial Designation C 16–20). Where this test was not considered sufficiently severe, it was modified. The results are shown in Table IV.

TABLE IV

RESULTS OF LOAD TEST (Percent deformation)

Series	Standard A. S. T. M. test. 25 lbs. per sq. in. at 1350°C for 1½ hrs.	25 lbs. per sq. in. at 1400°C for 1½ hrs.	50 lbs. per sq. in. at 1450°C for 1½ hrs.	50 lbs. per sq. in. at 1500°C for 1½ hrs.
A	—	—	1.77	—
B	0.0	—	—	2.85
D	0.0	—	—	—
D–K	0.0	0.0	Failed	—
D–F	0.0	0.0	Failed	—
G	0.0	—	—	3.90
F	0.0	—	—	—

It was shown that all the bricks tested could withstand the standard A. S. T. M. Load Test. The failures occurring in the clay bonded mullite bricks (Series D–K and D–F) were evidenced by a diagonal shearing of the bricks. That this was due to the softening of the bond is borne out by the fact that the pure cyanite brick (A) did not fail under the equally severe test of 50 pounds per square inch at 1450°C.

Softening Point The softening point test was carried out according to a method used by the Bureau and known as the A. S. T. M. Standard Method, Serial Designation C 24–20. The determinations in terms of cone numbers are shown in Table V.

TABLE V

RESULTS OF SOFTENING POINT TEST

Series	Composition	Remarks
A	Pure cyanite	Remained rigid at cone 35
B	Pure mullite	Remained rigid at cone 35
D-K	Mullite + 25% ball clay	Remained rigid at cone 36
D–F	Mullite +25% fire clay	Softened between cones 36 and 37

No attempt was made to determine the exact softening point of the pure cyanite or mullite. The ability of the pure material to remain rigid at cone 35 was sufficient to show that the life of the pure brick in actual service would be excellent so far as refractoriness is concerned.

Absorption The absorption was determined on specimens cut from the brick and weighing not less than 100 grams. The absorption data are shown in Table VI and compare favorably with those obtained on well-fired fireclay brick.

TABLE VI

ABSORPTION OF FIRED BRICK

Series	A	B	D	D–K	D–F	G
% Absorption	14.3	18.2	19.9	16.9	15.2	14.9

Resistance to Spalling The resistance to spalling was determined by a quenching method which followed in principle the tentative A. S. T. M. method. It consists in heating the bricks at one end of a kiln door to 850°C and plunging them half way into running water. The bricks are allowed to remain in the water three minutes, taken out, allowed to steam in the air for five minutes, and then returned to the kiln door. The process is repeated in hourly cycles until the entire end of the brick has spalled off or can be easily removed with the fingers, which is interpreted as failure. Five bricks of each series were quenched and the results are reported in Table VII as the average number of quenchings required to produce failure.

TABLE VII

RESULTS OF QUENCHING TEST

Series	Number of quenchings from 850°C to running water
A	O. K. after 60 (test discontinued)
D–K	O. K. after 73 (test discontinued)
D–F	O. K. after 73 (test discontinued)
G	Failed after 6 quenchings
B	Failed after 29 quenchings

There is no evident reason for the failure of bricks of series G (75% cyanite and 25% fire clay) after only six quenchings. The failure of bricks of series B, after 29 quenchings, may be due to the fact that they were bonded with a proprietary brand of material instead of a gum solution, for it was noted that they developed small cracks while drying. However, they were fired along with the rest of the series for completion of the data. The results, therefore, are not strictly comparable. The cyanite brick of series A bonded with gum, and the clay bonded mullite bricks of series D–K and D–F, exhibited excellent resistance to spalling.

Thermal Expansion A 1x1x6-inch bar of calcined cyanite (mullite and siliceous glass) was found to expand uniformly from 20° to 1000°C[1] with a coefficient of 0.0000056. The curve is shown in Fig. 1.

Resistance to Slagging A slag erosion test as developed at the Bureau and described by Geller[2] was conducted upon bricks of series A, D–K, and D–F to determine the relative resistance of the bricks to the combined action of molten slag and flue gases at high temperatures.

A test chamber approximately 24 x 24 x 4½ inches inside was built into a laboratory kiln. The test bricks formed a baffle wall against which the flame from a compressed air burner impinged. This flame carried with it finely-ground slag introduced through a refractory tube by a slow stream of air just above the burner and so directed that the slag was distributed upon the crest of the flame impinging on the test panel.

The interior of the kiln was brought to 850°C and maintained at this temperature throughout the test by means of the burners at the side which are used regularly in firing the kiln. The temperature of the interior of the test chamber was raised to 1450°C by means of the compressed air burner and maintained there for four hours, during which time four pounds of slag were gradually introduced through the refractory tube as described.

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[1] For description of method used, see forthcoming "Second Progress Report of the Investigation of Sagger Clays," by R. A. Heindl. U. S. Bureau of Standards.

[2] R. F. Geller, "Testing of Fireclay Brick with Special Reference to Their Use in Coal-Fired Boiler Settings." U. S. Bur. Stand., *Tech. Paper*, No. 279, page 127.

The finely-ground slag, falling into the flame was picked up, the finer grains were melted almost instantly and the entire charge was carried against the test bricks in the cover of the test chamber. The slag flowed down across the face of the test panel at the back and was retained in the pocket at the bottom while the flame swept on and down to the recuperator through two flue holes left in the side walls of the test chamber.

The slag had a softening point of 1100°C and was prepared in the laboratory by calcining and grinding (to pass 100-mesh) the proper raw materials to approximate a high sulphur, low fusing coal ash of the following composition:[1]

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3
30.7	19.6	18.9	1.1	11.3	3.7	1.9	0.5	12.2

The bricks showed only slight signs of erosion, comparing favorably with the most resistant clay brick. It is possible that the slag as prepared was not corrosive enough in its action to produce comparable results.

Conclusion

Mullite, pure, or bonded with clay, produced refractory bodies capable of withstanding standard and modified laboratory tests for high grade refractories. The bodies were highly refractory and showed excellent resistance to deformation under load and to spalling. They also showed a uniform rate of thermal expansion. In general the results obtained to date indicate that, with commercial quantities of the pure mineral available, the prospects for the development of mullite as a so-called "super-refractory" appear very bright.

Acknowledgments

The author wishes to express his appreciation to Herbert Insley for petrographic examinations, to H. C. Stecker for chemical analyses and to Nelson D. Booth for assistance in the preparation and testing of the specimens.

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[1] Analysis obtained from Bur. Mines, *Bull.*, No. 209, p. 2.

CYANITE-CLAY REFRACTORIES—I[1]

By H. C. Harrison[2]

ABSTRACT

The dissociation of cyanite into mullite was studied. Bricks were made of various mixes and their properties are given. Twenty per cent is about the minimum amount of clay which will give the proper bond. It was found desirable in some cases to add MgO in small amounts to promote a crystalline bond between the dissociated cyanite grains and the bonding material. In Pt. II the phase rule equilibrium relations are discussed.

Previous Work

Previous to 1923, sillimanite was supposed to be the stable high temperature form of Al_2O_3–SiO_2 and it was thought that cyanite and andalusite having the same composition inverted to this phase at temperatures from 1320° to 1380° C.[3] About this time, Bowen and Greig of the Geophysical Laboratory published the findings of their investigation of the system Al_2O_3–SiO_2.[4] This work showed that sillimanite had no stable range at high temperatures although it was very inert and unaffected by heating to any temperature below 1545° C. The work also proved the existence of the compound $3Al_2O_3$–$2\ SiO_2$ which was named mullite and showed that the isomeric minerals sillimanite, andalusite, and cyanite, all dissociate at high temperatures into mullite and either silica or a highly siliceous glass.

In a later paper J. W. Greig reported the results of a study of the "Formation of Mullite from Cyanite, Andalusite, and Sillimanite."[5]

In this work, Greig reports that cyanite alters at the lowest temperature of any of the three minerals and that

> in the cases of cyanite and of andalusite the alteration commences on the surfaces of the grains and advances inward. In that of sillimanite the change seems to take place throughout the grain.
>
> When andalusite and sillimanite are decomposed, the newly formed mullite crystals are oriented parallel to the original crystals; with cyanite this orientation is determined by the surfaces from which the mullite grows.
>
> In all three cases the new phases formed are of lower density than the original mineral so there is an expansion accompanying the decomposition.

Peck[6] has reported the results of an investigation into the possibility of using cyanite, andalusite, and sillimanite as ceramic raw materials.

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[1] By permission of the Director Bureau of Mines. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division). Received March, 1926.

[2] Coöperative Research Engineer, Bureau of Mines, Ceramic Experiment Station, Columbus, O.

[3] Dana. A System of Mineralogy.

[4] *Jour. Amer. Ceram. Soc.*, **7** [4], 238 (1924).

[5] *Jour. Amer. Ceram. Soc.*, **8** [8], 465 (1925).

[6] *Jour. Amer. Ceram. Soc.*, **8** [7], 407 (1925).

In his summary he concludes that due to the large expansion accompanying the dissociation of cyanite and the friable nature of the resulting product, it is unsuited for use as a ceramic material unless it is previously calcined to a temperature above its dissociation range.

The Raw Material

The cyanite with which this investigation is concerned is from a deposit occurring near Pamplin, Va. The rock from which the mineral is concentrated contains roughly 25% cyanite and 75% quartz. In addition to these two principal minerals there is a small percentage of rutile and a very small amount of mica. The rock near the surface also carries iron oxide as a stain on the surface of the other minerals. The color of the cyanite varies from a blue (or blue-green due to the yellow iron stain on the surface), to a very pale gray. The yellow iron stain which gives the cyanite a green cast may easily be removed by washing with acid revealing the blue color of the cyanite. The nature of the rock varies from a rather friable coarse-grained mass containing a large percentage of quartz and deep colored crystals of cyanite to a fine-grained fibrous mass which is tough and contains a high percentage of cyanite varying from slightly colored crystals to crystals which are practically white.

The rock after being crushed and ground is concentrated (tabled) for use. The following is a chemical analysis of the cyanite concentrate upon which the major part of the work was done.

Ignition loss	0.27%	CaO	0.10
Al_2O_3	58.62	MgO	0.24
SiO_2	38.54	K_2O	0.00
Fe_2O_3	1.54	Na_2O	0.25
TiO_2	0.64	Mean sp. gr.	3.57
P_2O_5	0.02		

When figured to mineral composition this analysis represents 93% cyanite and 4% quartz together with 3% of accessory minerals.

Dissociation Studies

A study of the dissociation of cyanite was made on the first sample of concentrate received which, unfortunately, was not as high grade as that upon which the subsequent work was done. This concentrate showed the following analysis:

SiO_2	45.18	CaO	none
Al_2O_3	52.08	MgO	0.11
Fe_2O_3	1.82		
TiO_2	0.40		99.87
P_2O_5	0.28	Mean sp. gr.	3.46

The analysis figures to be about 83% cyanite and 14% quartz.

The screen analysis of the material as received was:

Screen mesh	Per cent	Screen mesh	Per Cent
On 20	3.2	on 48	14.2
" 28	29.6	" 65	3.3
" 35	48.5	Through 65	1.0

The calcines for the dissociation study were made in a vertical cylindrical platinum wound resistance furnace. The furnace core of alundum was 15 inches long and 1 inch inside diameter with a wall thickness of ⅛ inch. The heating unit is externally wound on this tube for approximately 9 inches of its length. A uniform temperature zone about 3 inches long was located and all calcinations were run in this zone.

Some of the concentrate as received was ground wet for 68 hours in a porcelain jar mill to 100% through 300-mesh.

The calcines were made up by placing about 12 grams of the concentrate as received in a nickel crucible of the J. Lawrence Smith type. A second crucible was then set on the material in the first and about 12 grams of the finely-ground concentrate placed in it. A platinum, platinum-rhodium thermocouple hot junction was embedded in the powder contained in the upper crucible. The crucibles were then suspended in the furnace and heated in about 2½ hours to the desired temperature, which was then maintained for one-half hour. At several of the temperatures a second calcination was made in which the temperature was maintained for five hours. Specific gravity determinations were run on the calcined powder by the pycnometer method. The results of this study are shown in Fig. 1.

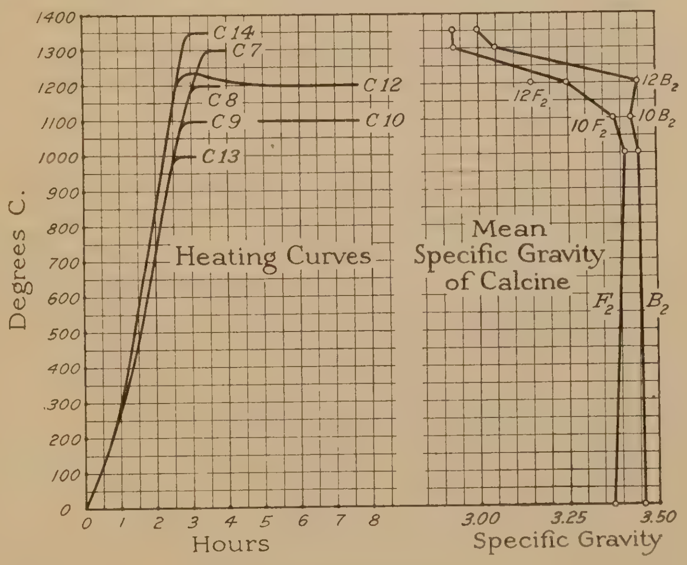

FIG 1.

In Fig. 1, the heating curves for the different runs are given, designated by a C and the number of the run. At the right of the figure the curves for the mean specific gravity of the calcines are given. The curve for the coarse material is marked B_2 while that for the fine material is marked F_2. The values obtained when the temperature was maintained for one-half hour are the points used to establish the curve. The results obtained when the temperature was maintained longer than one-half hour are indicated as points with the calcine number and letter indicating the grain size.

The values for the specific gravity of the 300-mesh concentrate were lower than those for the coarse material even before being calcined due probably to contamination from the grinding process but this is of no significance as the purpose of these tests was to establish the effect of grain size on the temperature and rate of volume change.

The curves seem to indicate that with fine material the dissociation starts and is completed at somewhat lower temperatures than with the coarser concentrate. This is to be expected from the findings by Greig whose work was published after these tests were completed. He states that the dissociation starts at the surface of the cyanite particles and progresses to the center. It would therefore be expected that increased surface and decreased volume would hasten the dissociation.

The specific gravity curves seem to indicate that with the coarse concentrate the dissociation progresses rapidly at about 1300°C but is not complete even at 1350°C. The dissociation of the fine material tends to be less abrupt than the coarse and is complete before 1350°C. No reliable quantitative results were obtained on the effect of time on the dissociation due to the hump in curve C12. Point 12 F_2 would have lain nearer the specific gravity curve if it had not been for the hump in the heating curve. The indication is that time is not so vital a factor as is temperature in governing the rate of inversion above the initial reaction temperature.

Bond Clay Tests

After considering the various clays available for bonding the concentrate in making brick, it was decided to use those with high alumina contents. This type was chosen with the idea of keeping the Al_2O_3 content of the refractory as high as possible. Four diaspore clays and three Georgia bauxitic clays were used in the study. All of them were "short," that is, not highly plastic.

The trials were made by grinding the clay to a thick slip and mixing with the concentrate, then dewatering the batch on plaster protected by muslin. When sufficiently dry the batches were granulated and dry pressed into briquets $2 \times 1 \times \frac{1}{4}$ inches at a pressure of 2900 pounds per square inch. Trials of each batch were fired to cone 14, 20, 26, and 30. The linear shrinkage and the fired porosity of each trial was determined.

With the type of clays used and with fine ground uncalcined concentrate, the trials seemed to indicate that 10% clay gave insufficient strength either in the dry unfired state or when fired to cone 14, the lowest temperature at which it was assumed that the dissociation would probably be complete. With increased grain size, more and more bond clay was required until with mixes containing particles which just passed a 20-mesh screen, about 40% clay on the calcined basis was required to give the briquets a promising strength when fired at the temperature employed.

The properties of the briquets did not vary a great deal with the different clays used. The results obtained with one of the Georgia bauxitic clays (G–14), which was later chosen for use in making up some of the bricks, is given below as a characteristic example of the properties of the briquets. (See Table I.)

The grain size number indicates the mesh of the screen that the largest particle of concentrate in that particular batch will just pass and from this the particles grade down to the fines. The batch marked "K" indicates that the concentrate has been calcined. The grain size of this batch corresponded with number 28. The mean specific gravity of this calcined concentrate was 3.01. The composition of batch number 14, the one given was Georgia bauxitic clay, 32% and cyanite concentrate, 68%. This gives an alumina-silica ratio of slightly over 1 to 1.

Analysis of the bauxitic clay used:

Moisture at 105°C	.46	P_2O_5	0.01
Loss on ignition	25.41	CaO	0.31
SiO_2	14.42	MgO	0.12
Al_2O_3	56.23	K_2O	0.00
Fe_2O_3	0.93	Na_2O	0.06
TiO_2	2.34	Sulphur	0.06
			100.35
		Deformation (cone)	39

The results of these trials showed that raw concentrate could be used satisfactorily and that a body made of the calcined concentrate would change very slightly in firing from the molded size.

The results in the above table also showed that the expansion upon firing of the test pieces containing raw concentrate varied greatly with the grain size of this material.

TABLE I

(Al_2O_3—63% SiO_2—34%)

Firing Temp.		Cone 14		Cone 20		Cone 26		Cone 30	
Grain size	Mix no.	Expansion %	Porosity %	Expansion %	Porosity %	Expansion %	Porosity %	Expansion %	Porosity %
K	14	−1.0	36.6	−2.0	32.7	−2.0	31.0	−3.0	31.5
20	14	11.4	49.9	10.0	45.3	10.4	44.3	7.5	43.3
28	14	9.0	46.4	7.5	44.4	8.5	41.3	5.0	40.3
35	14	7.5	47.2	4.0	43.0	6.0	42.0	2.0	36.5
48	14	7.0	45.9	3.0	39.5	4.5	39.9	0.0	34.8
65	14	2.5	39.0	1.0	35.9	2.5	36.7	−2.5	29.9
100	14	1.5	40.5	−0.5	34.3	1.0	35.9	−4.0	27.6

Bricks of Raw Cyanite and Bauxitic Clay

A screen analysis of the raw materials showed that the grain size of the concentrate did not range uniformly from the largest size to the smallest but that a large percentage of the particles was relatively coarse and another large percentage was quite fine, while there was only a small percentage of particles of intermediate sizes. The following screen analysis is typical:

Screen	Per cent retained on	Screen	Per cent retained on
28	0.0	100	0.6
35	31.5	150	4.5
48	27.7	200	4.8
65	3.7	200	27.2 through

Bricks were made up by the same method as the briquets only that they were formed at a pressure of about 600 pounds per square inch. The results of the first series of bricks made up with bauxite clay for bond showed when raw concentrate was used the brick containing cyanite coarser than 28-mesh did not fire successfully due to the volume change in the cyanite. They also showed that at least 20% of this particular clay must be added to give sufficient bond to the brick.

If the above precautions were not followed the brick showed an undue tendency to crack upon firing. Presumably this was due to the elbowing of the particles during the expansion of the raw cyanite at the dissociation temperature. Also, it was found that if the firing temperature was raised too rapidly through the dissociation range, which was assumed to be between cones 7 and 14, the bricks showed a decided tendency to crack and be punky. With all the brick containing 28-mesh raw concentrate, seven to eight hours or more were required to pass successfully through the dissociation range. Several attempts were unsuccessful when only two to three hours were allowed. In some of the later brick which were made with smaller grain sizes this point was not so important due to the more gradual dissociation induced by the greater surface exposed by the cyanite particles.

The first successful bricks contained raw concentrate and were made up as described above. They were fired to cone 30 observing the above precautions. The properties of these brick are given in columns 1 and 2, Table II.

TABLE II

	68% concentrate (93% cyanite) (raw) 32% Ga. bauxitic clay (G14)	68% concentrate (93% cyanite) (raw) 32% Ga. bauxitic clay (G14)	68% concentrate (93% cyanite) (calcined) 32% Ga. bauxitic clay (G14)
Per cent Al_2O_3–SiO_2 ratio (fired basis)	SiO_2 34 Al_2O_3 63	SiO_2 34 Al_2O_3 63	SiO_2 34 Al_2O_3 63
Maximum grain size	28-mesh	48-mesh	28-mesh
Firing temp.	Cone 30	Cone 30	Cone 18
Firing time	32 hrs.	32 hrs	33 hrs.
Av. linear expansion on firing %	5.56*	2.33*	.16**
Porosity %	45.6*	43.0*	47.43**
Load test 25 lbs. per sq. in. %	1½ hr. at 1500° C 6.85 contraction	1½ hr. at 1500° C 4.0 contraction	1½ hr. at 1500° C 3.25 contraction***
Spall test % (standard) 1350° C	Total loss 10 immersions 18.5	Total loss 10 immersions 22.7	Total loss 8 immersions 11.95***

* Average for 3 bricks.
** Average for 10 bricks.
*** Average for 2 bricks.

In the hope of making a refractory which would be more commercially possible, a number of brick were made up by the same method as the above and of the same composition but using calcined cyanite concentrate which showed a mean specific gravity of 3.04 and of the following screen analysis:

Screen no.	Per cent retained	Screen no.	Per cent retained
28	0.0	100	9.6
35	32.2	150	5.1
48	31.9	200	1.9
65	11.8	200	7.5 through

These brick were fired to cone 18. Their properties will be found in column 3, Table II.

A study of thin sections of the above brick was made. This seemed to indicate that there had been little action between the cyanite particles or their dissociation products and the refractory bond. The particles were merely imbedded in a more or less sintered mass of clay bond. In the case of the brick made with raw concentrate the character of the dissociated cyanite particles could be observed. As described by J. W. Greig, the crystals of mullite formed during the dissociation are parallel and extend into the original particle perpendicular to the surface. When crystals from two adjacent surfaces meet, their growth apparently stops and as the dissociation continues with its accompanying expansion, a crack opens up at the edge of the particle. Thus each particle is split into six smaller particles and any sectional view shows four of them somewhat similar to a Maltese cross.

Unfortunately there seems to be no intergrowth or interlocking of the mullite crystals but rather an opening up of pores extending into the center of the particle from each edge. Even in the case of brick made from calcined concentrate, the particles of dissociated cyanite are imbedded in the clay as in the above case with no apparent action between the two. The clumps of smaller particles formed by the dissociation as described above are in some cases clinging together while in others the smaller particles have been separated and are entirely surrounded by clay.

Fluxes to Induce Crystal Bond

As shown in the table of properties, all of the above brick have a very high porosity. In the hope of reducing this porosity and of promoting a secondary growth of crystals in the brick during firing, a study was made of fluxes which might be added to the batch. In this connection three batches were made up of:

(1)	Cyanite concentrate	66.7%
	Al_2O_3 (calcined)	33.3%

(2) No. 1 batch to which was added 0.5% of MgO as such
(3) No. 1 batch to which was added 0.5% of CaO as such

These three batches were ball milled for an extended period and cast into test bars. The batches were figured to contain about 72% Al_2O_3 with the remainder SiO_2 and fluxes. This composition is slightly over the mullite ratio. Upon firing to cone 20 the batch containing no added flux and the one containing CaO were very similar, both showing an apparent porosity of approximately 21%. The batch containing 0.5% MgO fired at the same time showed a much higher shrinkage and apparent porosity of less than 3%.

Some of the properties of the batch containing the 0.5% MgO are shown below in Table III.

TABLE III

Temp. of firing	Bar no.	Firing shrink. (per cent)	Apparent porosity (per cent)	Modulus of rupture (lbs./sq. in.)
Cone 12	1	0.5	51.97	2602
	2	0.5	50.65	4110
	3	0.5	51.67	3237
Cone 14	1	3.5	44.93	2528
	2	3.0	45.62	2208
	3	4.0	41.81	2965
Cone 16	1	7.0	37.37	2487
	2	7.0	36.92	3029
	3	7.0	36.00	2825
Cone 17	1	12.5	22.59	10960
	2	12.5	24.07	10880
	3	11.5	26.49	3488 bar checked
Cone 18	1	19.0	1.05	18440
	2	19.0	2.10	15370
	3	18.5	2.67	13450
Cone 23	1	20.5	2.62	14330
	2	18.0	0.41	5225 bar checked
	3	18.5	0.09	12110

Bricks were made up by the same method as described previously. The screen analysis of the concentrate used was very similar to the one given in Table II for the bricks which contained raw concentrate. MgO and CaO were added to these mixes with bauxitic clay as shown in Table IV. In another series diaspore was used as the bonding material, results of which are shown in Table V.

The analysis of the Missouri diaspore clay used in the brick in Table V is:

Moisture at 105°C	0.07%	P_2O_5	0.44%
Ignition loss	5.03	CaO	0.26
SiO_2	17.34	MgO	0.37
Al_2O_3	68.84	Na_2O	0.51
Fe_2O_3	1.16	K_2O	1.48
TiO_2	4.02		
			99.52

As will be seen, the attempt to lower the porosity by these methods failed. This was due doubtless to the relatively coarse nature of the brick mix.

The next attempt to produce a brick of lower porosity was by finer grinding of the concentrate and using ball clay as the bonding material the analysis of which is:

Kentucky Ball Clay		Kentucky Ball Clay	
Water at 212°F	14.23%	CaO	none
SiO_2	61.32	MgO	1.50
Al_2O_3	22.46	Alkalis	0.34
Fe_2O_3	0.15		100.00

TABLE IV

	68% concentrate (93% cyanite) (raw) 32% Ga. bauxitic clay (G14) 0.5% MgO	68% concentrate (93% cyanite) (raw) 32 % Ga. bauxitic clay (G14) 0.5% CaO	68% concentrate (93% cyanite) (calcined) 32% Ga. bauxitic clay (G14) 0.5% MgO
Al_2O_3–SiO_2 ratio (fired basis) %	SiO_2 34 Al_2O_3 63	SiO_2 34 Al_2O_3 63	SiO_2 34 Al_2O_3 63
Maximum grain size	28-mesh	28-mesh	28-mesh
Firing temp.	Cone 20	Cone 20	Cone 20
Firing time	75 hrs. av.	75 hrs. av.	75 hrs. av.
Av. linear expansion on firing (%)	7.35*	7.1*	−1.55*
Porosity (%)	49.91*	50.7*	37.95*
Load test 25 lbs. per sq. in. %	2 hrs. at 1450 C 5.81 contraction	2 hrs. at 1450 C 5.56 contraction	1½ hrs. at 1500 C 3.73 contraction warped 0.15″ center
Spall test (standard) 1350° C %	Total loss 8 immersions 36.86	Total loss 2 immersions 32.44	No appreciable loss on 10 immersions

* Average for 2 bricks

TABLE V

Composition (per cent raw basis)	80% concentrate (93 cyanite) (raw) 20 Mo. diaspore clay	72% concentrate (93 cyanite) (raw) 28 Mo. diaspore clay	80% concentrate (93 cyanite) (calcined) 20 Mo. diaspore clay	72% concentrate (93 cyanite) (calcined) 28 Mo. diaspore clay
Al_2O_3–SiO_2 ratio (fired basis) %	SiO_2 35 Al_2O_3 61	SiO_2 33 Al_2O_3 62	SiO_2 35 Al_2O_3 61	SiO_2 33 Al_2O_3 62
Maximum grain size	28-mesh	28-mesh	28-mesh	28-mesh
Firing temp.	Cone 20	Cone 20	Cone 20	Cone 20
Firing time	75 hrs. av.	75 hrs. av.	75 hrs. av.	75 hrs. av.
Av. linear expansion on firing (%)	11.05*	10.0*	0.55*	0.4*
Porosity (%)	48.25*	48.0*	38.1*	38.35*
Load test 25 lbs. per sq. in. (%)	2 hrs. at 1370° C 4.51 contraction	2 hrs. at 1370° C 2.6 contraction		1½ hrs. at 150 C° 2.68 contraction
Spall test (standard) 1350° C (%)	No appreciable loss 10 immersions	No appreciable loss 10 immersions	Total loss on 4 immersions 22.70	No appreciable loss 10 immersions

* Average for 2 bricks

TABLE VI

	80% concentrate (93% cyanite) (raw) 20% Ky. ball clay	80% concentrate (93% cyanite) (calcined) 20% Ky. ball clay	80% concentrate (93% cyanite) (raw) 20% Ky. ball clay + 3% talc	80% concentrate (93% cyanite) (calcined) 20% Ky. ball clay + 3% talc	80% concentrate (93% cyanite) (raw) 20% Ky. ball clay + 3% talc	80% concentrate (93% cyanite) (calcined) 20% Ky. ball clay + 5% talc
Al_2O_3–SiO_2 ratio (fired basis)	SiO_2 44% Al_2O_3 53%	SiO_2 44% Al_2O_3 53%	SiO_2 45% Al_2O_3 51%	SiO_2 45% Al_2O_3 51%	SiO_2 45% Al_2O_3 51%	SiO_2 45% Al_2O_3 51%
Maximum grain size	65-mesh	65-mesh	65-mesh	65-mesh	65-mesh	65-mesh
Firing temp.	Cone 20	Cone 20	Cone 20	Cone 20	Cone 20	Cone 20
Firing time	35 hrs.	35 hrs.	35 hrs.	35 hrs.	35 hrs.	35 hrs.
Av. linear expansion on firing	3.75%*	−2.9%*	1.35%*	−3.15%*	0.45%*	−3.75%*
Porosity	31.5%*	25.8%*	26.2%*	25.2%*	23.6%*	21.85%*
Load test 25 lbs. per sq. in.	1½ hr. at 1500 C 0.8% contraction					
Spall test from 850° C	25 immersions no loss	25 immersions cracked badly but no pieces could be removed	6 immersions half of end removed by fingers	25 immersions end removed 15% of brick	25 immersions end removed 15% of brick	6 immersions half of face removed
Fusion		Cone 36		Cone 35		Cone 33

* Average on 2 bricks

To some of these ball clay bonded brick, talc was added to supply magnesia as a flux. The analysis of the talc used was:

Loss on ignition	5.71	CaO	5.69
SiO_2	57.43	MgO	27.78
Al_2O_3	2.14	K_2O	0.49
Fe_2O_3	0.59	Na_2O	0.14
P_2O_5	0.08		
TiO_2	0.06		100.11

The properties of these brick are given in Table V. Bricks shown in column 1 Table V showed better in the laboratory test than any other bricks made in this study. The bricks containing the talc did not show up well in the spall test. This may have been due to the lime in the talc which was present as tremolite.

The data shown in Table VI was an attempt to make a brick of near the mullite ratio of alumina to silica with a low porosity. As can be seen from the table of properties the attempt was not entirely successful.

TABLE VII

48.7% concentrate (93% cyanite) (raw) 51.3% Mo. diaspore clay + 0.5% MgO		48.7% concentrate (93% cyanite) (raw) 51.3% Mo. diaspore clay + 0.5% MgO	
Al_2O_3–SiO_2 ratio (fired basis) %	SiO_2 28 Al_2O_3 66	Firing time	35 hrs.
		Av. linear expansion on firing (%)	1.6*
Max. grain size	65-mesh		
		Porosity	41.8*
Firing temp.	Cone 20		
		Load test 25 lbs. per sq. in.	1½ hr. at 1500° C 2.5% contraction
		Spall test from 850° C	25 immersions hair line cracks on end

* Average on 2 bricks

Effect of Low Grade Cyanite

In order to get some idea of what could be expected of a lower grade concentrate, the brick in Table VIII were made with cyanite of the following analysis:

Ignition loss	0.30%	CaO	0.80
SiO_2	47.26	MgO	0.08
Al_2O_3	49.82	Na_2O	0.03
Fe_2O_3	1.16	K_2O	0.00
TiO_2	0.92		
P_2O_5	0.01		100.38
		Mean sp. gr.	3.42

This analysis figures approximately 79% cyanite and 18% quartz.

TABLE VIII

	80% concentrate (79% cyanite) (raw) 20% Ky. ball clay	80% concentrate (79% cyanite) (raw) 20% Ky. ball clay
Al_2O_3–SiO_2 ratio (fired basis) (%)	SiO_2 52 Al_2O_3 46	SiO_2 52 Al_2O_3 46
Maximum grain size	65-mesh	65-mesh
Firing temp.	Cone 20	Cone 16
Firing time	30 hrs.	30 hrs.
Av. linear expansion on firing (%)	4.21*	5.65**
Porosity (%)	35.91*	38.5**
Load test 25 lbs. per sq. in. (%)		2 hrs. at 1450° C 1.9 contraction**
Spall test (%)	from 1350° C total loss 5 immersions 18.18 from 850° C total loss 21 immersions 11.00	

* Average on 6 bricks
** Average on 2 bricks

In the case of the bricks shown in Table IX the concentrate showed the following analysis:

SiO_2	49.54%
Al_2O_3	45.52
Fe_2O_3	2.45
TiO_2	1.94
Total	99.45

which indicates 72% cyanite and 23% quartz.

TABLE IX

	80% concentrate (72% cyanite) (raw) 20% Ky. ball clay		80 concentrate (72% cyanite) (raw) 20% Ky. Ball clay
Al_2O_3–SiO_2 ratio (fired basis) (%)	SiO_2 53 Al_2O_3 42	Firing time (hrs.) Av. linear expansion on firing (%)	30 4.65*
Max. grain size	65-mesh	Porosity (%)	34.87%*
Firing temp.	Cone 20	Spall test (%)	From 1350° C total loss 5 immersions 17.73 From 850° C total loss 18 immerisons 12.

* Average on 4 bricks

The brick in Tables VIII and IX were made of the same composition as brick in Table VI without flux, that is, 80% concentrate and 20% Kentucky ball clay. The table shows the effect of an increasing amount of quartz on the properties of the brick.

All of the low temperature spall tests (850°C) were heated in the door of an electric furnace (nichrome resistance type). The effect of atmosphere was accordingly absent.

Microscopic Examination

A microscopic examination of thin sections of brick made up with ball clay indicated that there was a slight tendency for the clay to react with the calcined cyanite particles and also that a very fine structure tended to develop in the clay between the particles. (See Fig. 2.)

In the brick made up with ball clay and with MgO added as talc for a flux, the thin sections showed considerable reaction between the clay and the altered cyanite particles with the development of mullite crystals in non-parallel orientation extending from the edges of the particles into the clay between them. In the cases where the larger amount of talc was used (see Fig. 2), the mullite crystals above mentioned were relatively gross and well developed.

In the cases where MgO was added as such to refractory clays it seemed to be relatively inaccessible and the desired structure did not show up.

Slag Resistance

The old A.S.T.M. tentative slag test was run on the brick whose compositions and properties are shown in columns 1, 2, and 6, Table VI and in Table VII. Acid and basic open hearth slag were used in the tests. These tests failed to differentiate between the several mixes in a satisfactory manner except where the porosities were very close. It showed however that all the bricks tested were more resistant to acid than to basic open hearth slag as would be expected. All bricks with a porosity of over 35% absorbed slag very readily. All the bricks tested with a porosity of less than 30% resisted slag well. Due to the unsatisfactory character of the test method no quantitative relations can be given.

We are indebted to Mr. Powell of Stone and Webster for certain laboratory slag tests run in accordance with his Company's impingement test. The slag used was Illinois coal ash. The tests were carried out at 2900°F. The results are shown in Table X.

TABLE X

Sample no.	Composition per cent	Per cent remaining	Per cent porosity
3	Pure cyanite–ball clay $52.5Al_2O_3$–$43.5SiO_2$	74.8	32
4	Impure cyanite–ball clay $42.0Al_2O_3$–$52.5SiO_2$	49.8	35
C–2	Impure cyanite–kaolin $49.0Al_2O_3$–$49.0SiO_2$	77	26
A–2	Pure cyanite–diaspore $67.0Al_2O_3$–$30.0SiO_2$	72.0	32

Samples No. 1 and No. 2 are from the same mix as brick, the properties of which are shown in column 1, Table VI and Table IX.

Sample No. 3 was made from an 80% cyanite concentrate and bonded with a hard Georgia kaolin. Sample No. 4 was from a 95% cyanite concentrate bonded with finely-ground diaspore.

Sample No. 2 showed up least well due largely to its higher porosity and low alumina content, and in part to the ball clay bond.

The other three samples showed surprisingly little difference in their ability to stand up under the test in spite of the wide variation in alumina content.

Mr. Powell reports that in cone fusion tests on slag-refractory mixes the best results were obtained on the sample approaching the mullite ratio (No. 4).

Results on extensive service tests are incomplete but appear to favor diaspore-cyanite mixes where slag erosion is the major service requirement and the clay-cyanite mixes for resistance to spalling, under the conditions of the tests.

EQUILIBRIUM CONSIDERATIONS OF CYANITE-CLAY REFRACTORIES—II

BY W. J. MCCAUGHEY[1] AND H. C. HARRISON

It has been shown by Greig, as stated before, that cyanite when heated between 1300 and 1350°C dissociates very rapidly into mullite and free silica, the latter probably as the mineral cristobalite.[2]

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[1] Chairman, Dept. of Mineralogy, Ohio State University.

[2] In the discussion following, the quantitative relations can be obtained diagrammatically with a millimeter scale using the lever reaction and while reasonably accurate are only approximately so. For the application of the lever reaction, see paper by Rankin and Wright (Ternary System $CaO.Al_2O_3.SiO_2$) *Amer. Jour. Sci.*, **39**, 53 (1915), line 28 *et seq.*

100 lbs. cyanite = 87.7 lbs. mullite + 12.3 lbs. cristobalite

The mullite formed in this reaction has the characteristic needle habit and the lengths of the crystals are perpendicular to the outside surface of the cyanite crystal fragment. The interstitial spaces between the mullite needles carry the cristobalite.

Upon further heating, the cristobalite and a small part of mullite react at a temperature of 1545°C to form a melt of composition 94.5% SiO_2 and 5.5 Al_2O_3.

12.3 lbs. cristobalite + 1 lb. mullite = 13.3 lbs. melt

leaving 86.7 pounds of mullite undissolved. Upon further heating according to the diagram published by Bowen and Greig this liquid would dissolve progressively more mullite with consequent enrichment in alumina. The amount of mullite dissolved and the composition of the resultant melt would depend upon the temperature to which the mixture has been heated. As the development of mullite proceeds the cyanite fragments develop a peculiar hour glass structure as shown by Greig and as mentioned before.

The small amount of melt formed at 1545°C and its high viscosity does not favor the melt coming together to form larger masses and producing deformation. If impurities are present in the cyanite this melting phenomenon will take place at a lower temperature.

The melt formed lies between the tiny needles of mullite and does not seem to come to the surface of the grain probably because of the high viscosity of the melt and because of the capillarity of the intercrystalline space.

In order to convert the cyanite to 100% mullite composition it would be necessary to add alumina in the proportion of 32 pounds of alumina to 100 pounds of cyanite. The cheapest source of alumina would be diaspore clays, but on account of the silica content of diaspore clay it would be necessary to add more of it than if pure alumina were used.

Microscopic examination shows that when diaspore clay is used to overcome the high silica content of cyanite to form mullite, only a part of alumina-silica melt reacts with the diaspore to form the mullite. The latter mineral forms around the periphery of the cyanite grain helping to form a matrix or bond for the calcined cyanite particles. The greater part of the high silica glass enclosed between the mullite crystals is not accessible for reaction with alumina probably due to the high viscosity of the glass. Finer crushing would render more of the glass available; the same effect would be produced by the addition of some substance to change the composition of the glass and consequently lower its melting temperature and viscosity.

For this purpose magnesium oxide was added to the cyanite-diaspore mixture. Microscopic examination shows that both fine grinding and addition of magnesium oxide does make available more of the high silica glass for reaction with the diaspore to form mullite. The interstitial spaces between altered cyanite particles show abundant, well developed and comparatively large crystals of mullite in nonparallel orientation. The mullite seems to start from the edges of the altered cyanite particles and grows in all directions into the interstitial spaces.

The equilibrium data in Fig. 2 and in the appended tables is from papers published by Geophysical Laboratory. Rankin and Merwin, *Amer. Jour. Sci.*, **45**, 301 (1918). Bowen and Greig, *Jour. Amer. Ceram. Soc.*, **7** [4], 238-54, [5] 410 (1924).

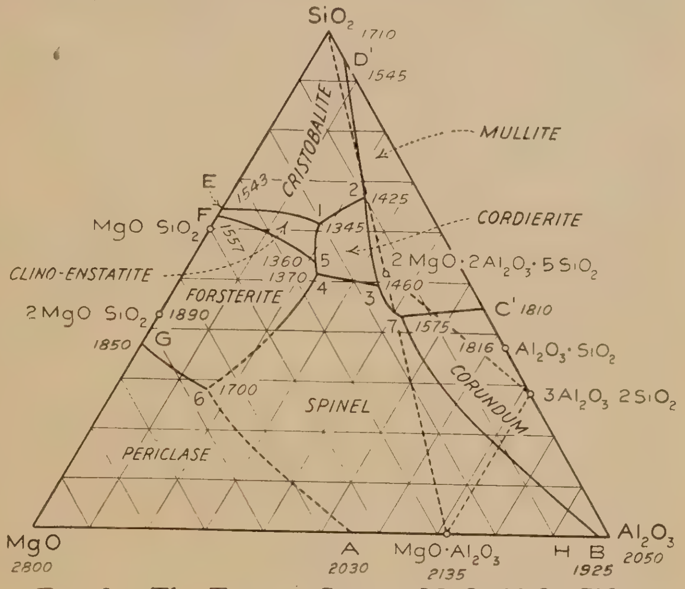

FIG. 2.—The Ternary System $MgO–Al_2O_3–SiO_2$.

TERNARY INVARIANT POINTS

Phases	MgO	Al_2O_3	SiO_2	Temp.
1. $MS–S–M_2A_2S_5$	20.3	18.3	61.4	1345
2. $S–A_3S_2–M_2A_2S_5$	10.0	23.5	66.5	1425
3. $A_3S_2–MA–M_2A_2S_5$	16.1	34.8	49.1	1460
4. $MA–M_2S–M_2A_2S_5$	25.7	22.8	51.5	1370
5. $M_2S–MS–M_2A_2S_5$	25.0	21.0	54.0	1360
6. $M_2S–M–MA$	56.0	16.0	28.0	1700
7. $A–MA–A_3S_2$	15.2	42.0	42.8	1575

BINARY INVARIANT POINTS

A	Periclase MgO Spinel $MgO\cdot Al_2O_3$	45	55		2030
B	Spinel Corundum	2	98		1925
C′	Corundum Mullite		55	45	1810
D′	Mullite Cristobalite		5.5	94.5	1545
E	Cristobalite Clino-enstatite	36		64	1543
F	Clino-enstatite Forsterite	37.5		62.5	1557

Phases	MgO	Al_2O_3	SiO_2	Temp.
G Forsterite Periclase	63		37	1850
COMPOUNDS				
Periclase	100			2800
Corundum		100		2050
Cristobalite			100	1710
Spinel $MgO \cdot Al_2O_3$	28.4	71.6		2135
Forsterite $2MgO \cdot SiO_2$	57.1		42.9	1890
Clino-enstatite $MgO \cdot SiO_2$	40		60	
Cordierite $2MgO \cdot 2Al_2O_3.5SiO_2$	13.7	34.9	51.4	
Mullite $3Al_2O_3 \cdot 2SiO_2$		71.8	28.2	
Cyanite $Al_2O_3 \cdot S_1O_2$		62.8	37.2	

In the $MgO–Al_2O_3–SiO_2$ diagram (see Fig. 2) it will be seen that mullite may be a part of the three sub systems.

(*a*) Mullite–cordierite–cristobalite
(*b*) Mullite–cordierite–spinel
(*c*) Mullite–spinel–corundum

All positive mixtures of mullite, cordierite, and cristobalite will have compositions (in MgO, Al_2O_3 and SiO_2) which lie within the triangle formed by drawing straight lines between the compositions of these three crystal phases. Conversely all compositions (of MgO, Al_2O_3 and SiO_2) that lie within this triangle will consist of the three crystal phases cristobalite, cordierite, and mullite when equilibrium is attained. This same reasoning follows for the other two composition triangles.

Into which of these composition triangles the cyanite refractory falls will depend upon how much alumina and magnesia are added.

If a small amount of MgO (equal to or less than 4.25) is added to cyanite, the composition of the resultant mixture will lie in the mullite, cordierite, cristobalite composition triangle. The only melt that can form and be in equilibrium with these three crystal phases is represented by point 2 on the Rankin and Merwin diagram (Fig. 2). This melt has the composition MgO 10, Al_2O_3 23.5, and SiO_2 66.5, and is liquid at 1425°C.

If 2.5% of MgO is added to cyanite about 25% of the mixture melts at 1425°C, the composition of the melt is represented by point 2 and the undissolved residue is mullite. Further heating of this mixture will bring about the solution of some of the undissolved mullite, and the composition of the bond will change, becoming richer in alumina and poorer in silica due to the solution of the mullite.

If less than 2.5% MgO is added, a melt of composition 2 is formed as before, but the undissolved residue is now mullite and a small percentage of cristobalite. Upon further heating, the composition of the melt changes from point 2 following along the line 2D′ until the free silica is entirely dissolved. The change in composition of the melt is due to a solution of the free silica (cristobalite) and the mullite in proportion of about 12.3 SiO_2 to 1 mullite. The bond (or melt) thereby becomes richer in silica and more refractory until the free silica disappears. As the magnesia content in cyanite mixtures is lowered the amount of melt 2 formed will be consequently reduced and the further melting will bring the composition of the melt farther up the line 2D′ until in the case where no MgO is added there will be no melt 2 formed at all but the composition of the melt will have moved to D′ composition, 94.5% SiO_2 and 5.5% Al_2O_3. The amount of binary eutectic D′ formed from the pure cyanite refractory now becomes 13.3% and its melting point 1545°C, whereas when 2.5% MgO is used 25% of melt is formed which is of a less refractory nature (melting point 1425°C) and whose composition is represented by point 2. Intermediate additions of MgO from 2.5% to zero produce corresponding results both in amount and refractoriness of the bond.

The addition of MgO to cyanite in amounts more than 2.5% and up to 4.25% will make the bonding substance (melt) change its composition along the line 2–3 becoming poorer in SiO_2 and slightly richer in magnesia without much change in melting temperature. The amount of the bond formed with 4.25% of MgO increases to 28%.

In general, in that part of the MgO–Al_2O_3–SiO_2 system which forms the composition triangle, silica, mullite, and cordierite, the effect of additions of MgO to cyanite is to increase the amount of bonding melt, to lower its melting temperature, and to change the composition of the bond to a much lower SiO_2 content, thereby decreasing its viscosity. The addition of 2.5% of MgO to the cyanite increases the eutectic bond from 13.5% to 25%; the further addition of MgO to 4.25% increases the eutectic bond by a much smaller amount to only 28%.

The addition of alumina to cyanite adds to the refractoriness of the mixture, forming thereby more mullite and decreasing the amount of the Al_2O_3–SiO_2 eutectic formed. The effect of the addition of alumina and magnesia simultaneously (without taking the composition out of the composition triangle, silica, cordierite, mullite) is to change the composition and viscosity of the bonding melt. The addition of magnesia makes possible a bond of much lower SiO_2 content and therefore lower viscosity. The lower viscosity will permit a larger growth of mullite needles and consequent development of a gross structure in the fired body. The lower viscosity should also permit of decreasing the amount of bond required and permit increased formation of mullite by the addition of considerable alumina without making the material too refractory for manufacture. It is possible, therefore, to vary the character of the material by varying the amount of alumina and MgO additions. Of course, it is understood that these equilibrium conditions are only approximately approached in commercial bodies because of the lack of fine pulverization and the immaturity in firing. However, with their continued use in practice at high temperature, equilibrium conditions are more nearly attained.

Whenever the composition of the mixture is brought close to mullite by the addition of Al_2O_3 to cyanite the further addition of MgO throws the composition of the system into the composition triangle composed of mullite, cordierite, and spinel. In such cases the bonding melt which forms first and which can be in equilibrium with these minerals has the composition of point 3 in the $MgO–Al_2O_3–SiO_2$ diagram of Rankin and Merwin. In this composition triangle spinel is one of the end members instead of free silica. Spinel does not however contribute much to the formation of the melt. Approximately 100 pounds of cordierite react with 8 pounds of spinel and 100 pounds of melt are formed and 8 pounds of mullite crystallize out in the process of forming melt 3. Mullite therefore is not only not fluxed in this process but actually is formed by the reaction

100 lbs. of cordierite + 8 lbs. spinel = 100 lbs. melt "3" + 8 lbs. mullite

Cordierite ($2MgO\ 2Al_2O_3\ 5SiO_2$) is the mineral which contributes most to the formation of melt 3. As more melt is required the composition of the system should be moved closer to cordierite; if less melt is required the composition of the system should be moved away from cordierite and toward the composition of mullite or toward the composition of spinel according to whether a refractory is desired in which either mullite or spinel is the predominant mineral. All of the cordierite will melt at the temperature 1460° if there is enough spinel to react with it.

If the temperature is raised still higher the composition of the silicate bond changes along the line 3–7 by solution of variable amounts of mullite and spinel. At 1575°C the melt has the composition of point 7 and the undissolved residue is mullite and spinel. Further heat treatment at this temperature will bring about a reaction between undissolved spinel and mullite crystals to form corundum and melt of composition 7 and without change in temperature according to the reaction as follows:

74 lbs. mullite + 26 lbs. spinel = 48 lbs. melt + 52 lbs. corundum

If the composition of the original system lies to the right of a line drawn from point 7 to the Al_2O_3 apex of the triangle the spinel will disappear first, and on further heating the composition of the melt will travel along the line 7–C′ with further crystallization of corundum and solution of mullite.

If on the other hand the composition of the original system lies to the left of the line joining 7 and Al_2O_3 apex of the triangle the mullite will disappear first, and upon further heating the composition of the melt will travel along line 7B with solution of both spinel and corundum in a ratio, varying according to the temperature. The amount of the melt formed depends on the temperature reached and the original composition of the system. The closer the composition lies to a line joining the composition of mullite and spinel the less will be the amount of cordierite in the system and less the amount of melt present in the system at any particular temperature; consequently the more refractory the system will be. It is a simple matter to calculate graphically by the lever reaction the amount of melt, if the original composition of the system is known and the composition or temperature of the melt formed in the reaction is known.

Sufficient alumina and MgO when added to cyanite will bring the mean composition of the mixture within the composition triangle composed of spinel, mullite, and corundum. The melt formed and in equilibrium with this system at 1575°C will have the composition of point 7 and will be formed by interaction of mullite and spinel, forming in the process of melting crystals of corundum as follows:

74 lbs. mullite + 26 lbs. spinel = 48 lbs. melt + 52 lbs. corundum

As before, the corundum does not contribute anything to the formation of the melt but actually crystallizes out in the melting process. The closer the original composition lies to point 7 the more melt is formed at this temperature; the farther away from point 7, that is, the less mullite the less melt is formed at 1575°C and the more refractory the system. The latter case would be of course more applicable to high alumina refractories such as diaspore.

If the original composition of the system lying within the composition triangle corundum, spinel, mullite, lies to the right of line joining 7 and the Al_2O_3 apex of the triangle the spinel will be the first mineral to be completely dissolved in the melt, mullite, and corundum forming the undissolved residue. On further heating the mullite passes into solution with concurrent crystallization of corundum and the composition of the resultant melt follows the line 7–C′. If the original composition lies to the left of the 7–Al_2O_3 line the mullite disappears at point

7 leaving an undissolved residue of corundum and spinel and on further heating the composition of the melt passes along line 7B, the spinel and the corundum both passing into solution into the melt in variable ratio depending upon the temperature.

On heating, those compositions which lie within the cristobalite, mullite, and cordierite triangle the only phenomenon noted is a melting or a solution phenomenon and subsequent recrystallization on cooling. Except for the melting of the eutectic this is a slow and gradual process, the melt changing its composition with increase in temperature.

In the cordierite, mullite, spinel system, and more especially in the mullite, corundum, spinel system there is (in addition to the melting and recrystallization phenomena on heating and cooling) an additional factor of importance, that is, the reaction of mixtures of mullite and spinel on heating at a temperature of 1575°C to form a liquid and the further crystallization of corundum. The structure developed at a lower temperature is destroyed by the interaction of the mullite and spinel to form a large amount of additional melt at a definite temperature (as distinct from a range in temperature) and recrystallization of the matrix to form considerable quantities of corundum (nearly equal in amount to the amount of increase in the melt). On cooling the system through this temperature, 1575°C, a new line-up of crystals would take place again, caused in this case by resorption of corundum and recrystallization of spinel and mullite from the melt. This change in structure at this temperature would cause profound changes in the structure of the brick if placed in use over a range of temperature which would include 1575°C. To overcome this sudden change in state at 1575° it would be necessary to change the composition of the system so that it would contain a very small amount of either spinel or of mullite. That is, a corundum-mullite refractory should contain only a little spinel (magnesia) and a spinel corundum refractory should contain only a little mullite (silica) if it is to be used over a range in temperature covering 1575°C.

Future Work

While the full effects of the above reasoning will not be attainable in the manufacture of a refractory due to certain practical limits as to grain size and temperature of firing, nevertheless, our thin section study has shown that a bond has developed along predictable lines and indications are that in service the equilibrium will be more nearly approached.

A series of cyanite bearing refractories has been made up and are now in service with much higher alumina (diaspore) content than any here reported. Some of these refractories contain MgO up to 3%. A report will be made on these series of refractories in the near future.

THE EFFECT OF ATMOSPHERIC CONDITIONS ON THE LOAD TEST FOR REFRACTORIES[1]

BY LEONARD FRANCIS SHEERAR[2]

ABSTRACT

The literature relative to the investigation was reviewed and criticized. Iron pyrite was added to clays in amounts varying from 0 to 5%. Test pieces 2 x 2 x 4½ inches were fabricated by the stiff-mud, and dry-press processes. After firing to cone 8 these were subjected to load tests at 1350°C under oxidizing, neutral, and reducing conditions. Expansion and contraction values were plotted against time and temperature. Results under reducing conditions. Expansion and contraction increased with increase of pyrite content.

Introduction

The load test as a means of judging the service of a refractory at elevated temperatures has been employed for several years. The American Society for Testing Materials has adopted a standard test,[3] which includes definite specifications regarding the type of furnace, method of heating and loading, size of test piece, and rate of heating. Nothing, however, is given regarding the condition of the atmosphere surrounding the test piece.

Fire clays contain up to 5% of iron-bearing minerals, whose most common and detrimental forms are limonite ($2Fe_2O \cdot 3H_2O$), siderite ($FeO \cdot CO_2$), and pyrite (FeS_2). Occasionally other compounds of iron are present. The injurious effect of these minerals is believed to be their reduction to the ferrous state with the resultant formation of ferrous silicates under reducing conditions. It would seem reasonable therefore that refractories will react differently under load, depending upon the kiln or furnace atmosphere, and an atmospheric clause should be inserted in the standard test. It was hoped that this investigation would throw some light upon these conditions.

Purpose of Investigation This investigation was undertaken to determine the effect of oxidizing, neutral, and reducing atmospheres on refractories under load at furnace temperatures. It was limited to the effect of atmosphere on the same clays with varying percentages of iron in the form of pyrite . In order to test the effect of the method of manufacture, the test pieces were made up by the soft-mud, stiff-mud, and dry-press processes.

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[1] Published with approval of the Director, U. S. Bur. Mines. This was a joint investigation of the U. S. Bureau of Mines and the Ohio State Univ. Eng. Expt. Station. The data given have been presented through the Department of Ceramic Engineering to the Graduate School at Ohio State Univ., as a thesis as part requirement for Master's Degree. Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Atlanta, Ga., Feb. 1926. (Refractories Division). Received January 12, 1926.

[2] Research Fellow at Columbus Station.

[3] Standard method of test for refractory materials under load at high temperatures. Amer. Soc. Test. Mat. Standards, 1921, pp. 617–621.

The Investigation

Raw Materials Table I gives analyses of the clays used, a Scioto-ville flint and a semi-flint clay from Grahn, Kentucky

TABLE I

ANALYSES* OF CLAYS USED

Constituent	Flint clay	Semi-flint
SiO_2	44.10	43.46
Al_2O_3	39.30	37.45
Fe_2O_3	1.80	1.19
TiO_2	2.00	2.44
CaO	0.25	0.27
MgO	0.40	0.49
Alkali	0.50	0.64
Ignition loss	13.80	14.08

*Analyses by D. J. Demorest.

Method of Preparation The pyrite added to the clay consisted of 50% passing through 20-mesh and retained on 35, and 50% through 35-mesh and retained on 80. No pyrite was added for the low-iron series, but 2.5% by weight was added for the medium iron and 5.0% by weight for the high iron.

The clays were put through a jaw crusher and rolls until they passed a 10-mesh screen. The dry-press specimens contained 75% flint and 25% semi-flint clay. They were thoroughly mixed in a Cincinnatus mixer, 10% of water being added to each mix. They were molded under a pressure of 2200 pounds per square inch.

The stiff-mud test piece contained 50% flint and 50% semi-flint clay. The water-clay mix was pugged and aged until it could be extruded through the steel die of a small brick machine, when it was wire-cut into briquets of the size stated below.

The soft-mud contained 50% flint and 50% semi-flint clay. The mix was thoroughly pugged with the proper amount of water to produce a soft mud. Specimens were then formed in wooden molds.

The size of the test specimens was 2x2x4½ inches. This particular size was chosen for the following reasons: (1) the temperature gradient in this size would be practically uniform through the cross-section; (2) the length would be enough to show any shearing stress developed; (3) a smaller cross-section would cause distortion by bending; and (4) this size is most appropriate for the load apparatus used.

Method of Firing The briquets were fired to cone 8 in a laboratory kiln in 48 hours under oxidizing conditions.

Testing

The tests were carried out in oxidizing, neutral, and reducing atmospheres in a furnace using a loading device similar to that described by Helser.[1] The rate of heating was that recommended by the A. S. T. M. During the progress of each run the slump was recorded in thousandths of an inch on an Ames dial. Figures 1 and 2 show the test pieces after the load test.

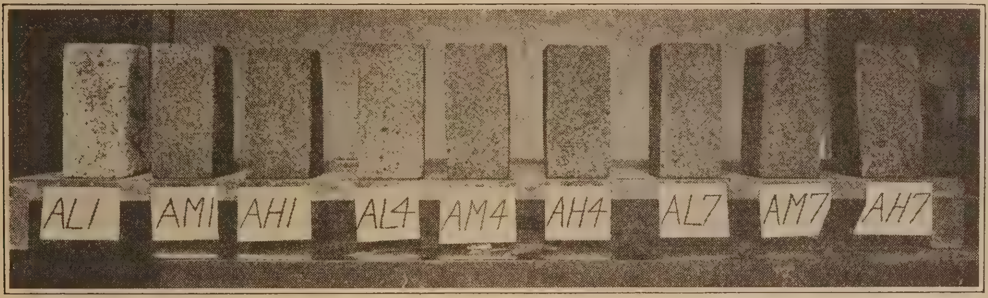

FIG. 1.

The oxidizing atmosphere was obtained by passing air through the muffle. Analysis of the exit gases under this condition gave less than 0.5% CO. A little CO was to be expected because of its formation in the carbon resistor and seepage through the muffle.

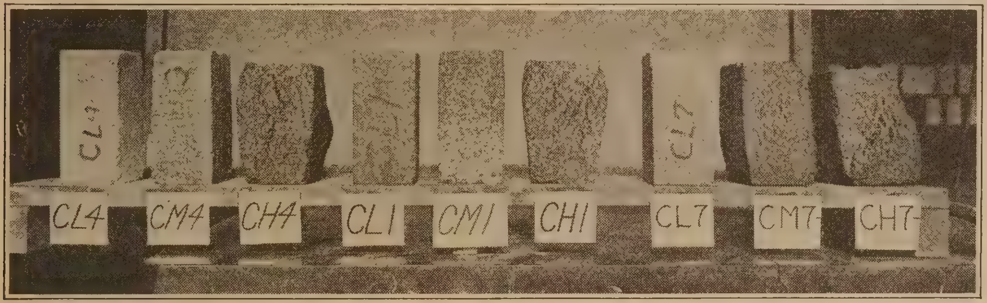

FIG. 2.

The neutral atmosphere was obtained by passing nitrogen gas through the muffle. The gas was passed through at a rate of 1 cubic foot per minute, and care was taken to keep the rate of gas flow constant in successive tests.

The reducing atmosphere was obtained by passing through the muffle, air that had previously been passed over charcoal at between 600 to 750°C. This gave a gas high in CO. The air was passed over the charcoal at a rate such that the atmosphere contained 10% CO, and by regulating the air flow and temperature of the charcoal it was possible to get an atmosphere containing exactly 10% CO throughout a test. Orsat analysis[1] of the furnace atmosphere was made every 15 minutes throughout the tests where a reducing atmosphere was maintained.

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[1] P. D. Helser, "A Laboratory Load Furnace," *Jour. Amer. Ceram. Soc.*, 8 [12], 822–25 (1925).

Figure 3 shows the load furnace and the tube furnace used for generating CO, and Fig. 4 is a cross-section of the load furnace with test piece in place.

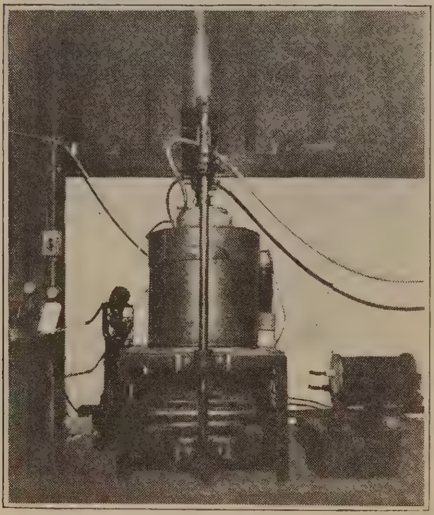

FIG. 3.

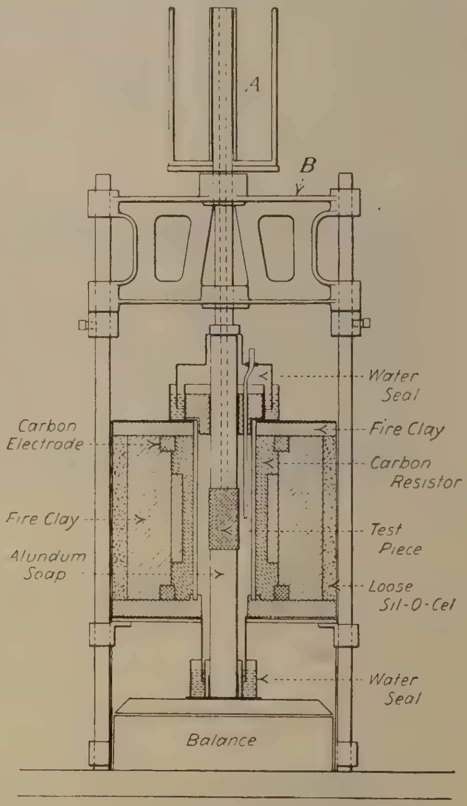

FIG. 4.

Results of Tests The curves of Figs. 5 to 13 inclusive show the contraction and expansion of the test specimens in tenths of an inch, and Table II gives the conditions and results:

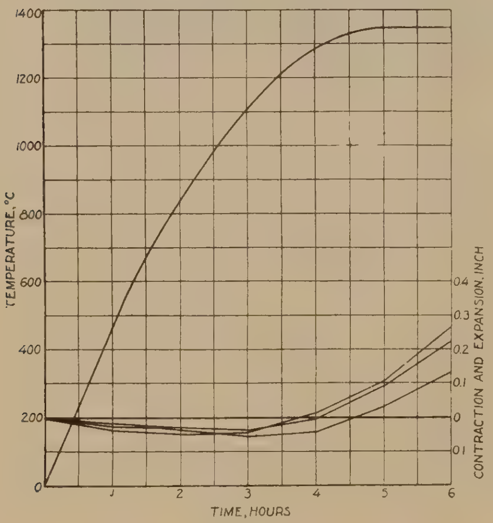

FIG. 5.

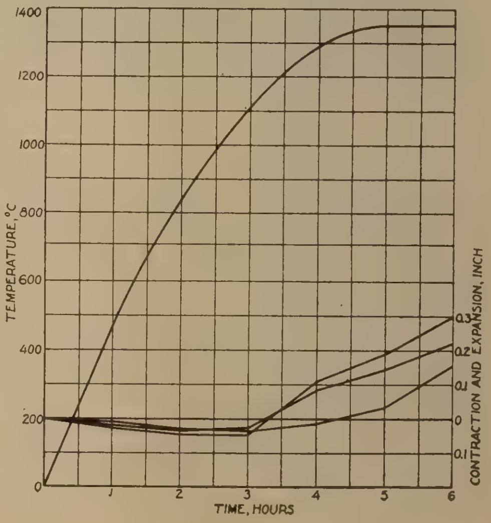

FIG. 6.

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[1] A. C. Fieldner, and G. W. Jones, "The Bureau of Mines Orsat apparatus." Bureau of Mines, *Tech. Paper*, **320**, 1926 (in press).

TABLE II
CONDITIONS AND RESULTS OF TESTS

Method of manufacture	Atmosphere	Pyrite added, per cent	Temperature expansion ceased and shrinkage began, °C	Total shrinkage 25 lbs. per sq. in., load at 1350°C per cent	Distortion under load at 1350°C
Soft-mud	Oxidizing	None	1100	3.0	None
“	“	“	1100	3.0	“
“	“	2.5	1050	5.1	“
“	“	2.5	1050	4.88	“
“	“	5.0	1000	6.0	Slight
“	“	5.0	1000	6.55	None
“	Neutral	None	1100	3.50	“
“	“	2.5	1000	4.80	“
“	“	5.0	1100	6.60	Slight
“	Reducing	None	1120	3.33	None
“	“	“	1120	3.33	“
“	“	2.5	1050	3.88	“
“	“	5.0	850	8.80	“
“	“	5.0	900	7.70	“
Stiff-mud	Oxidizing	None	1100	3.25	None
“	“	“	1100	3.35	“
“	“	2.5	1000	4.50	“
“	“	2.5	1050	4.50	“
“	“	5.0	900	4.75	“
“	“	5.0	920	5.50	“
“	Neutral	None	1100	2.50	None
“	“	2.5	1050	3.50	“
“	“	5.0	850	7.50	“
“	Reducing	None	1100	4.75	“
“	“	“	1120	4.62	“
“	“	2.5	850	5.6	“
“	“	2.5	950	6.0	“
“	“	5.0	700	8.0	“
“	“	5.0	900	8.0	“
Dry-press	Oxidizing	None	1100	1.3	None
“	“	“	1100	1.5	“
“	“	2.5	1000	5.3	Bloated
“	“	2.5	1000	5.5	“
“	“	5.0	950	Failed by shearing at 1200°	
“	“	5.0	950	Failed by shearing	
“	Neutral	None	1100	3.3	None
“	“	2.5	900	Run not completed	Bloated
“	“	5.0	700	Failed by shearing	
“	Reducing	None	1100	None	None
“	“	“	1100	2.1	“
“	“	2.5	1100	2.2	Slight bloat
“	“	2.5	1025	Failed before end of test	
“	“	5.0	900	Failed by shearing at 1200°	
“	“	5.0	925	Greatly distorted and sheared at 1200°	

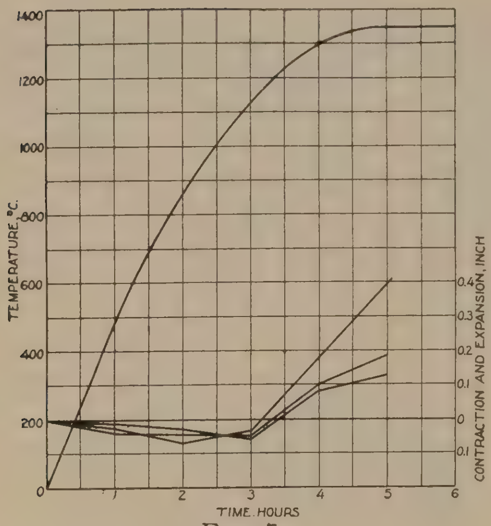


FIG. 7.

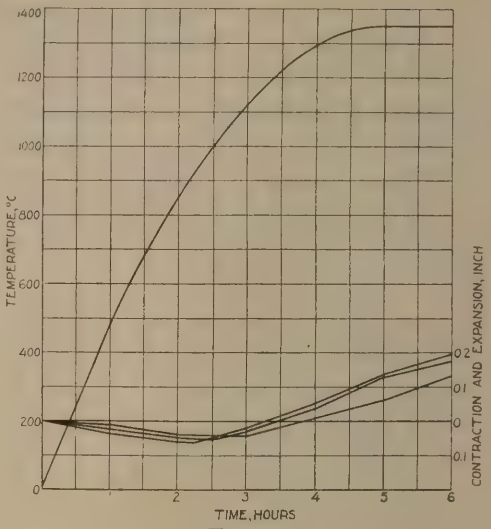


FIG. 8.

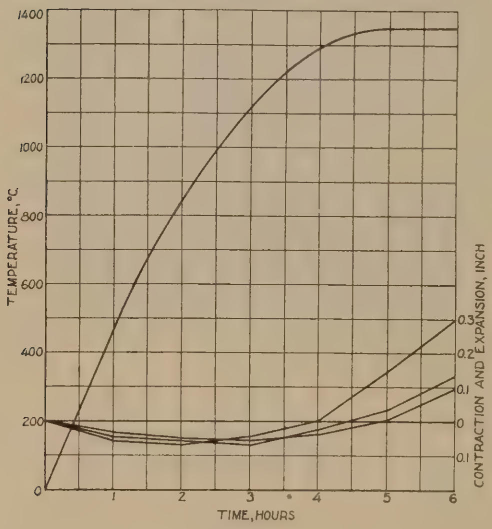


FIG. 9.

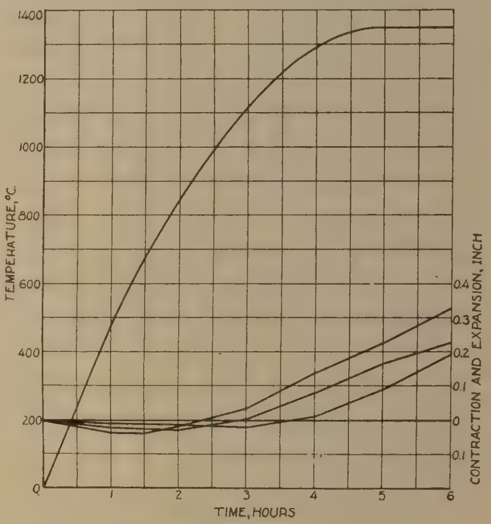


Fig 10 - Effect of reducing atmosphere at high temperature on stiff-mud specimens containing varying amounts of iron pyrite.

FIG. 10.

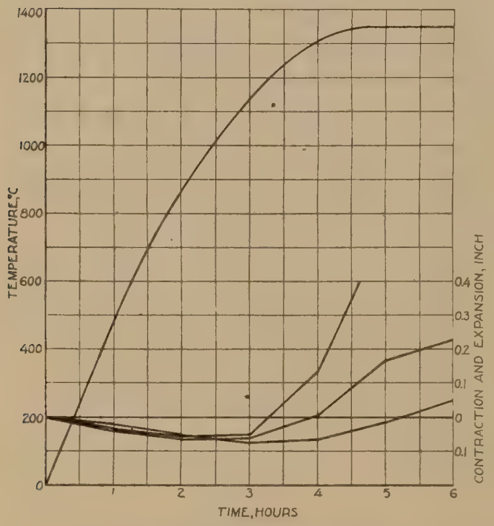


Fig 11 - Effect of oxidizing atmosphere at high temperature on dry-press specimens containing varying amounts of iron pyrite

FIG. 11.

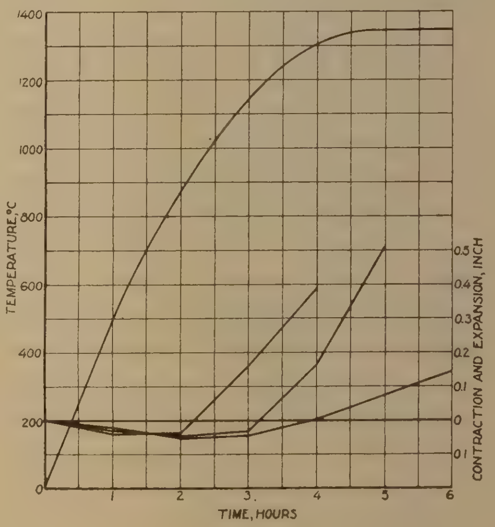
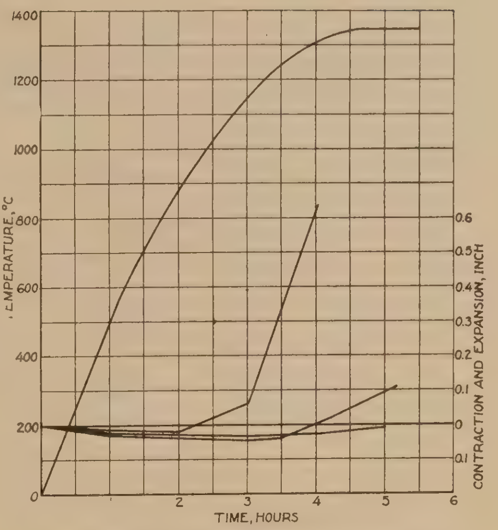


FIG. 12.

Discussion of Results



(Fig 13- Effect of reducing atmosphere at high temperature on dry-press specimens containing varying amounts of iron pyrite

FIG. 13.

A number of physical and chemical reactions take place when a refractory is heated under load, all of which may affect the results. However, as most of these variables have in this study been kept as near constant as feasible, we are concerned only with the effect of different atmospheres on pyrite in clay.

The magnitude of the effect of the different atmospheres depends upon a number of factors, as: (1) concentration of various gases in the atmosphere; (2) rate of penetration of the gases into the brick; (3) influence of time and temperature; and (4) pyrite content. This study has dealt with the effect of iron alone on the load-carrying qualities of refractory specimens, made by different processes and tested in different atmospheres.

As the temperature rises an expansion takes place, which continues until a point is reached where a well-defined contraction occurs. In every case the expansion and contraction increased with increasing iron content, and in every case high values were obtained in a reducing atmosphere, intermediate values in a neutral atmosphere, and low values in an oxidizing atmosphere.

The expansion in the different atmospheres did not vary greatly, but the contraction was accelerated in neutral and reducing atmospheres. Contraction began at lower temperature with increasing iron content.

It will be noted that the effect of atmosphere was most pronounced in briquets high in iron, as would be expected. The effect of the amount of iron present was also most pronounced in the case of the dry-press test pieces, irrespective of the atmosphere. Whether this effect is inherent in this process of manufacture, or whether the test pieces were not representative of the best practice, can not be concluded from these data. It would seem reasonable that an open ware would admit the reducing gases and so reduce the iron more readily than a dense ware. However, this does not explain the early failure of the dry-press ware high in iron under oxidizing conditions, and it would seem to indicate that no matter in what atmosphere, the principal cause of failure of the dry-press test pieces was the amount of iron present rather than the effect of the atmosphere.

Conclusions

1. A reducing atmosphere causes earlier and greater contraction at high temperatures in a fireclay refractory with a given iron content.
2. An increase in iron content causes an increase in expansion as the temperature is raised and a given atmosphere maintained.
3. An increase in iron content causes a contraction at lower temperatures in a given atmosphere.

Any conclusion in regard to the effect of method of fabrication should be reserved until further work is done on dry-press[1] pieces made up under varying conditions of grain size, moisture content, and pressure. A stronger plastic clay might easily reduce or eliminate the difficulty.

It would seem advisable to consider the service requirements demanded before submitting a refractory to tests, because lower strength and greater contraction under load will be obtained in reducing atmospheres than in either oxidizing or neutral atmospheres.

This study was limited to the pyro-chemical effect of pyrite on refractory specimens when tested in the three atmospheres under load conditions. Before definite conclusions could be drawn, a study of this sort should cover the effect of such other variables, as: (*a*) different bond clays; (*b*) original firing temperature; (*c*) effect of different forms of iron; and (*d*) more concentrated atmospheres. Because no analysis of observations was made on the chemical and physical changes in state of the pyrite and clay, theorizing does not seem justifiable as to the causes of the effects observed and here recorded.

The writer wishes to thank G. A. Bole, Superintendent of the Ceramic Experiment Station of the U. S. Bureau of Mines, and A. S. Watts, Professor of Ceramic Engineering in Ohio State University, under whose joint direction the tests were carried out. Acknowledgment is due to P. D. Helser for many suggestions, and to C. E. Bales of the Louisville Fire Brick Works for the clays used.

Review of Previous Investigations

This review of previous work has been subdivided under (1) Tests and Testing Apparatus, and (2) Effect of Gases on Fire Brick.

Tests and Testing Apparatus

1. **Action of Refractories under Load at High Temperatures.** LEMON PARKER. *Trans. Amer. Ceram. Soc.*, **7**, 185 (1905).—The first load test was made by Lemon Parker in 1905. While investigating gas-works fireclay tile said to have failed from undue shrinkage, he reasoned that failure was not due to excessive heat but to the load of the piers above. The results showed variation under load due to differences in composition and operation.

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[1] J. H. Kruson, and C. A. Smith, "The Manufacture and Physical Properties of Dry-press Brick," *Jour. Amer. Ceram. Soc.*, **8** [12], 829–32 (1925).

The work was of primary importance in that it proved the value of a requirement in refractories not before considered.

2. Tests on Fire Brick. M. Gary. *Mitteilungen aus dem kgl. Materialprüfungsamt*, **28,** 23–40 (1910). Abst. in *Jour. Iron and Steel Inst.*, **82,** 412 (1910).—Gary tested 55 kinds of fire brick. They were subjected to pressure of 7.5 to 10 kg. per sq. cm. He concluded that strength, compactness, and retention of shape depend mainly upon solidity of the grog, and that crushing strength is not proportional to specific gravity.

3. The Testing of Fireclay Refractories with Special Reference to Their Load-Carrying Capacity at Furnace Temperatures. A. V. Bleininger and G. H. Brown. U. S. Bur. Stand., *Tech. Paper*, **7,** 78 pp. (1911).—Tests were made with 50-lb. load at 1350°C. As the temperature rises the load carried must be decreased within the range of softening temperature. This temperature is lower the higher the fluxes, but seldom lower than 1150°C. With 75-lb. load and temperature of 1300°C the results were approximately the same, except that with a 50-lb. load at 1350°C the brick were more sensitive.

4. Effect of Loads on the Refractories of Fire Clays. J. W. Mellor and B. F. Moore. *Trans. Ceram. Soc.* (Eng.), **15,** 117 (1915).—These investigators assumed that a fire clay undergoes three different effects caused by pressure: (*a*) diminished apparent viscosity; (*b*) accelerated reactions; and (*c*) by change in melting point in accord with Clapeyron's rule. From their results obtained they concluded: (*a*) That the greater the load the lower the squatting temperature. (*b*) The decrease in the squatting temperature with unit increase of load is directly proportional to the squatting temperature and equal to k times the squatting temperature (k being a numerical constant). (*c*) The relation between squatting temperature T and load W in lb. per sq. in. is given by the expression $T = Ce^{-kw}$, where C = def. temperature (Seger cone) under no load, and e = exponential constant. (*d*) The more siliceous the clay the less difference between squatting temperature with and without load.

5. Modified Load Test for Fire Brick. J. B. Shaw. *Trans. Amer. Ceram. Soc.*, **19,** 498 (1917).—Shaw developed a furnace which he claimed was superior to the others in that the load decreased as the brick was crushed, thus allowing the brick to adjust itself to service conditions. The brick to be tested was placed in the furnace and fixed in position by compressing a spring until the desired pressure was obtained. Any contraction or expansion was recorded on coördinate paper.

6. Effect of Load on the Refractoriness of Fire Bricks. J. W. Mellor and W. Emery. *Trans. Ceram. Soc.* (Eng.), **17,** 360 (1918).—Tests were made on several types of refractories with much refined test conditions. The following conclusions were drawn: That fire bricks under load seemed to break down in one of two ways: (*a*) Fusion collapse whereby the bricks gradually give way as the temperature rises until the piece collapses. This behavior is typical of aluminous and zirconium bricks. (*b*) Mechanical failure, where the bricks show no evidence of gradual collapse but an abrupt collapse takes place. This is typical of silica, chrome, and magnesite bricks. Although the effects produced are exceedingly complex it would seem that inability to carry load, as is the case with so many of the other physical properties of fire clays, the composition of the material plays only a minor rôle; texture and porosity are the considerations of importance. It is probable that the matrix—that is, the more fusible constituent of the brick—determines the refractoriness under load, and as the mass gives way the whole collapses without being fortified by the grog.

7. A Machine for Testing the Hot Crushing Strength of Fire Brick. H. G. Schurecht. *Jour. Amer. Ceram. Soc.*, **2,** 602 (1919).—Schurecht developed a furnace and apparatus for which superiority in exactness was claimed.

8. A Possible Explanation of the Failure under Load at High Temperatures as Displayed by Fireclay Refractories. A. S. Watts. *Jour. Amer. Ceram. Soc.*, **3,** 448 (1920).—In 1920, Watts advanced the theory that the failure of fire bricks under load was perhaps not due entirely to the effect of fluxes, inferior bond clay, etc., but that it may be due in part to a physical weakness caused by the decomposition of the kaolin and recombination of Al_2O_3 and SiO_2 as sillimanite. Sillimanite developed in the original firing of the brick causes no weakness under load, but the sillimanite developed during the load test caused weakness.

9. Determination of the Compressive Strength of Fire Bricks at High Temperatures. E. Sieurin, F. Carlsson, and B. Kjellgren. *Ber. Deut. Keram.*, **3,** 53 (1921).—Refractoriness under load was defined as the temperature at which a test cube contracted 0.3% after heating for 2 hours under a pressure of 2 kg. per sq. cm. (28 lbs. per sq. in.). Cubes containing varying amounts of silica, alumina, iron oxide, lime, and magnesia, were examined. On increasing the silica, the minimum refractoriness occurred without load with 90% silica. On increasing the alumina, the refractoriness under load increased steadily up to 80% of alumina, when the test pieces failed suddenly, probably because there was not sufficient bonding clay present. An increase of 6.4% in the Fe_2O_3 (original content 0.89%) reduced the refractoriness under load 50°C. With further increase of Fe_2O_3, the refractoriness diminished more slowly and remained almost constant between 6 and 12% of Fe_2O_3, after which a further increase caused a rapid loss of refractoriness. On increasing the CaO content it showed a steady and rapid loss of refractoriness under load, an increase of 0.11% of CaO (original content 0.68%) reduced the refractoriness by 25°. The effect is less noticeable with coarse grog. MgO behaves similarly to CaO but the effect of very small percentages of MgO is greater.

10. Resistant Tests on Refractory Products under Load Conditions. V. Bodin. *Trans. Ceram. Soc.* (Eng.), **21,** 56 (1921).—The following conclusions were drawn: (*a*) The majority of refractories show a tendency to decreased resistance to load on heating, the minimum being about 600°C. (*b*) On further heating the same products exhibit rapidly increasing resistance with a maximum of about 1000°C. For certain clays this maximum may reach four times the minimum. (*c*) On further heating, a decline in resistance tending toward zero at about 1600°C is observed for all refractory products. (*d*) All refractory products tend to become plastic at about 1200°C.

Effect of Gases on Fire Brick

1. Effect of Gases on Fire Brick. Frank Firmstone. *Trans. Amer. Inst. Min. Eng.*, **34,** 427–31 (1904).—Firmstone discusses the effect of the action of carbonic oxide on iron in the fire brick of a furnace wall. Analysis of undecomposed portions of the lining gave the following:

Constituent	Glazed skin per cent	Body of brick per cent	Constituent	Glazed skin per cent	Body of brick per cent
SiO_2	40.23	57.63	MgO	4.31	0.11
Al_2O_3	12.22	31.64	K_2O	9.39	2.59
Fe_2O_3	14.93	3.73	Na_2O	8.43	0.51
CaO	10.92	0.24	Metallic Fe	....	1.51

The body of the brick was much stronger than new brick. No carbon deposits were visible and no carbon was found in the analysis. The iron oxide increased about 50% in the altered brick.

2. After Contraction and After Expansion of Fire Brick in Oxidizing and Reducing Conditions. J. W. Mellor. *Trans. Ceram. Soc.* (Eng.), **16,** 268 (1916).—Mellor investigated the magnitude of expansion and contraction of refractories in oxidizing and reducing conditions and noted the following effects:

Type of brick	Percentage after expansion or contraction	
	Oxidizing atmosphere	Reducing atmosphere
Silica brick, fine-grained	0.44 C	0.77 C
Silica brick, high in iron	0.58 E	0.48 E
Fire brick	0.21 E	Nil
Fire brick	Nil	0.33 E
Fire brick	1.12 C	1.27 C

C, contraction; E, expansion, cone 14.

According to Mellor these results indicate that silica brick give less expansion in a reducing atmosphere and fireclay brick have a greater contraction in a reducing atmosphere. These results are in agreement with the greater fluxing effect of iron in a reducing atmosphere. The magnitude of the fluxing effect of the reducing atmosphere depends upon (*a*) strength of reducing atmosphere; (*b*) rate of penetration of gases into interior of brick; (*c*) time and temperature.

3. The Influence of Oxidizing and Reducing Atmospheres on Refractory Materials. L. BRADSHAW AND W. EMERY. *Trans. Ceram. Soc.* (Eng.), **21**, 115 (1921).—Bradshaw and Emery noticed that Seger cones heated in an atmosphere of coal gas remained erect at temperatures far in excess of their ordinary softening temperatures. The cones were found to have a hard shell with a quantity of slag discharged at the base of a semi-vitrified mass covered with an infusible skin. In his investigation of Seger cones under various conditions, Rieke found that the melting points were affected by the rate and duration of heating as well as by the kind of atmosphere. Pieces of fireclay brick were heated in an atmosphere of coal gas and carbon deposition on the test pieces. Ferruginous material gave a reaction with the slag, bursting the cone.

4. The Disintegration of Refractory Brick by Carbon Monoxide. B. M. O'HARRA AND W. J. DARBY. *Jour. Amer. Ceram. Soc.*, **6**, 904–14 (1923).—Brick which showed disintegration in use were subjected to temperatures of 450 to 500°C and the brick which withstood CO were not affected at 1300°C. On examining the bricks, numerous iron spots, filled with sooty carbon, were noticed. Rupture was due to volume changes caused by the deposition of carbon. It would seem that an iron-free brick would be satisfactory in use, and to demonstrate this a series of tests was run on different refractories under atmospheres high in CO. The CO was generated by warming concentrated H_2SO_4 with formic acid and purified by absorbing CO_2 and O_2. Samples of the material were placed in Pyrex combination tubes and heated in a nichrome resistance furnace. The rate of passage of CO was from 0.1 to 1.0 liter per hour. Tests were made on four samples of fireclay brick, and the following results were obtained: (*a*) A fireclay brick subjected to CO for 29 hours at a temperature of 550° showed deposits of carbon and swelling and cracking around the deposits. (*b*) A second test run for 51 hours at 750°C showed less cracking, which shows that the effect of CO becomes less as the temperature rises. Its strongest action is at about 550°C. (*c*) Magnesite brick under similar conditions disintegrate the same as fireclay brick. Silica, chrome, and carborundum brick are not affected.

AN INVESTIGATION OF CHECKER BRICK FOR CARBURETERS[1]

By C. W. Parmelee and A. E. R. Westman[2]

ABSTRACT

A progress report of an investigation of checker brick for carbureters which is being conducted by the Department of Ceramic Engineering of the University of Illinois in coöperation with the gas companies of northern Illinois has been presented. The methods used in carrying out commercial and laboratory tests and the data so far obtained have been submitted for discussion and criticism. When the investigation has been completed a final report will be made.

I. Introduction

1. Object of the Investigation At the request of certain public utilities companies in the northern part of the state of Illinois, the Department of Ceramic Engineering at the University of Illinois undertook an investigation of the different types of checker brick that were on the market in order to find which types of checker brick gave the longest service in carbureters and to develop simple laboratory tests which could be used for predicting the probable life of a checker brick when used in a carbureter. In this investigation the utilities companies have coöperated with this laboratory to the fullest extent.

2. Description of the Operation of a Carbureter In the manufacture of carburetted water gas, a machine which consists essentially of a generator, a carbureter and a superheater is used. The carbureter contains a checker work of fire brick which is heated to a high temperature during the "blow" by secondary combustion of lean producer gas, which is produced from coal or coke in the generator. When the checker work has reached a sufficiently high temperature (1600°F to 2000°F in top courses), a "run" is made, during which steam is blown through the incandescent bed of fuel in the generator and the resulting "blue gas" is passed through the hot carbureter into which gas oil is sprayed. The heat of the checker work vaporizes the oil and "cracks" it into more volatile hydrocarbons which mix with the blue gas in the carbureter and superheater producing carbureted water gas, which has a higher B.t.u. value than the blue gas. During the run the carbureter cools to about 1200°F.

The checker brick are thus subjected to alternate heating and cooling, to alternate oxidation and reduction, to the disruptive action of the oil and steam and to the slagging action of the fuel ash.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division). Received Dec. 17, 1925.

[2] And their assistants W. H. Pfeiffer and A. J. Paul.

3. Recent Decrease in the Life of a Checker Brick The amount of carbureted water gas manufactured in the middle west has increased to such an extent in recent years that it is no longer possible to secure light distillate gas oils in sufficient quantities and recourse has been had to heavier and more impure grades of oil. This, in turn, has necessitated an increase in the operating temperatures of the carbureters and has caused an increase in the amount of coke and other impurities deposited on the checker work in the carbureters. Under these conditions, the checker work is rapidly choked up by the disruption of the upper courses of checker brick and by the deposition of coke and impurities from the oil, with the result that the time between shut-downs from this cause has decreased from about 4000 to about 500 operating hours. This effect is particularly pronounced in some of the carbureters in Chicago where as much as 8 or 10 inches of an asphalt-like material is deposited on the checker brick.

II. Commercial Tests

Procedure

4. Initiation of Commercial Tests As the first step in this investigation, a series of commercial tests of different brands of checker brick was initiated in the spring of 1925 at the gas plant of the Illinois Power and Light Company at Champaign and at the Crawford Avenue plant of the People's Gas, Light and Coke Company of Chicago. Some of these tests have been completed, others are in operation at the present time and a second series is planned.

5. Types of Checker Brick Investigated In choosing the brands of brick to be tested, an effort is made to include only those brands which differ to a considerable extent in structure and composition. Some fifteen brands of checker brick have been tested or are under test at the present time. Table I gives a summary of the data, which has been secured from the manufacturers, pertaining to the method of manufacture and the nature of the raw materials, etc., of these fifteen brands.

6. Measurements Made before Test Certain measurements are made on the bricks to be tested as they are received from the manufacturer. These measurements are used later (see Sect. III) in calculating the deterioration the bricks undergo during the test. Thus, the average modulus of rupture for each brand of brick is determined by the American Society of Testing Materials method for building brick (C21–20). The bricks to be placed in a carbureter are numbered with a refractory slip, a detailed description of each brick is noted and four measurements of its length (to $\frac{1}{32}$ inch) are made.

TABLE I

DATA SUBMITTED BY MANUFACTURERS

Brand	Location of plant	Raw materials	Method of manufacture	Firing temp. in cones
B	Missouri	2nd grade semi-flint and plastic	Dry press	
C	Missouri	Same as B	Stiff mud repress	
D	Pennsylvania		Dry press	
E	Illinois	Plastic clay	Stiff mud repress	9–11
F	Pennsylvania	Flint and plastic clays	Soft mud repress	
G	Missouri	Grog, flint, and plastic	Stiff mud repress	8
H	Missouri	Semi-flint	Stiff mud repress	10–12
I	Kentucky	Ky. flint and semi-flint	Hand mold, hand press	
J	Kentucky	Same as I	Stiff mud repress	11
K	New Jersey		Hand mold, hand press	12
L	Missouri	Cheltenham plastic	Dry press	8–10

7. Test Procedure When a carbureter is being recheckered, about fifty numbered bricks of each of three brands are assembled near the carbureter and used in setting two or more courses (the 1st and 2nd in Champaign, the 4th and 5th in Chicago); the brands are distributed in such a way that all will receive equal treatment and a chart showing the position, number and brand of each brick is made.

While the carbureter is in use (a period of 3 to 4 weeks), the gas company keeps a continuous record of the temperatures, duration of shutdowns, fuel consumption, output of gas, quality of oil and other operating data which might bear some relation to the behavior of the brick.

The next time the carbureter is shut down for recheckering, a description of the inside of the carbureter is recorded, the test bricks are identified by means of the chart (see above) and are renumbered as they are removed. The badly shattered bricks are placed in bags and the bags numbered. Samples are secured of any slag or asphalt-like material that may have been deposited in the carbureter.

8. Measurements Made after Test The length of the bricks which have been under test and which have not been badly cracked is measured, as before, to $\frac{1}{32}$ inch. A description of each brick that has been under test is recorded, the bricks are graded, using the photographs shown in Fig. 1 to define "good," "fair," and "poor" and "bad" condition, and the number in each grade noted

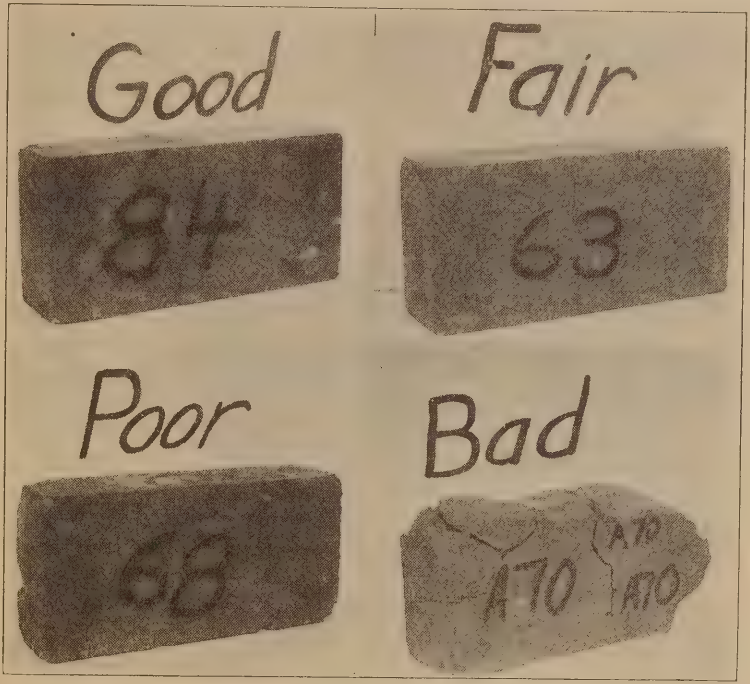

FIG. 1.

When this has been done, the bricks are laid out on the floor so that they occupy the same relative positions that they did in the carbureter and a photograph such as that shown in Fig. 2 is taken. Photographs illustrating the "average" and "typical failure" conditions of each brand are also taken. (See Fig. 3.)

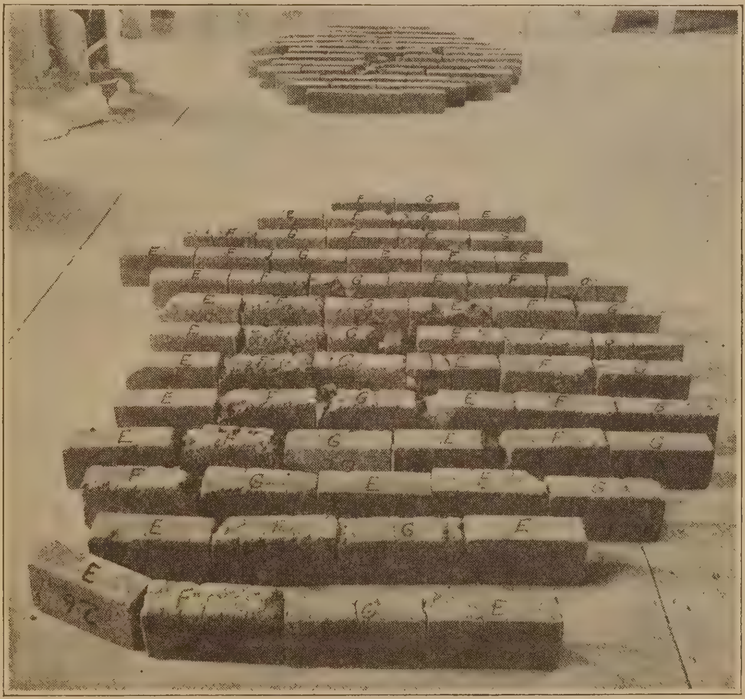

FIG. 2.

The modulus of rupture of each of the unbroken bricks of each brand is then measured and and average modulus of rupture for each brand obtained by dividing the sum of the moduli of rupture of the unbroken bricks by the total number of that brand in the test. This is equivalent to assigning zero strength to the broken bricks. The bricks are then stored pending microscopic examination and further tests.

III. Commercial Tests (Calculations)

9. Use of a Check Brand Since it is impossible to secure exactly the same condition in every test, due to unavoidable shut-downs, changes in quality of oil and fuel, etc., one brand of brick has been used in all the tests and the results of a test are calculated by comparing the behavior of the other brands in the test with the behavior of this check brand.

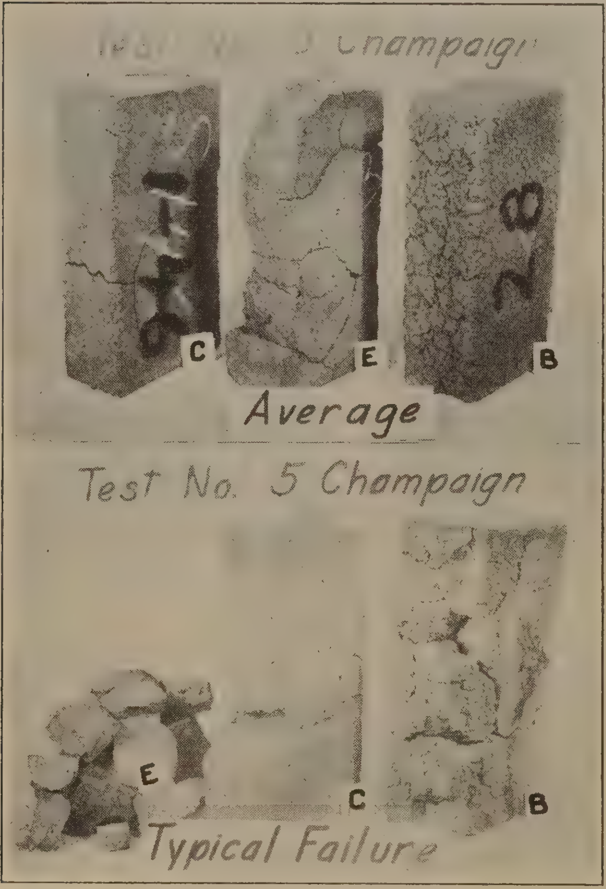

Fig. 3.

10. Equivalent Per Cent Decrease in Strength From the measurements of modulus of rupture made before and after each test the per cent decrease in strength of each brand is calculated. In the tests in Champaign the check brand suffers about 90% decrease in strength, the values for the first six tests being 91.6, 90.3, 88.1, 96.8, 93.4, and 93.5. To allow for the variation in the severity of the tests shown by these figures, the per cent decrease in strength of each brand is calculated to a basis of a 90% decrease in strength of the check brand. Thus the per cent decrease in strength of the brands in Test *I* would be multiplied by 90/91.6, etc. The number so obtained is called the "equivalent per cent decrease in strength" and serves as a measure of the amount of cracking in the bricks. As the modulus of rupture of a brick which is cracked through one-half its width is just one-quarter of that of a whole brick, the use of this number in this way tends to exaggerate the differences between brands.

11. Slagging and Erosion The appearance of the bricks that have been under test shows that the fuel ash from the generator, the coke breeze, and the asphalt-like deposits from the oil attack certain brands of brick much more than others. While the fraction of a brick which is lost by actual solution is not appreciable, yet the bloating, softening, and vitrification due to slag penetration often cause parts of the brick to shell off and produce surfaces favorable to the development of thick layers of asphalt-like material (see Par. 3). It was therefore deemed advisable to classify the bricks on the basis of their appearance after a test and to take this into consideration when deciding on the relative merits of the different types of brick when used in a carbureter. In classifying the brands of brick the following grades were used:

Grade A—the bricks are not noticeably penetrated by the slag
Grade B—the bricks show definite slag penetration but no important attendant effects (bloating, etc.)
Grade C—small fragments of the bricks have been lost due to slag penetration and subsequent erosion by coke breeze (B, Fig. 3)
Grade D—the bricks show penetration with noticeable attendant scaling and bloating
Grade E—the bricks show penetration with pronounced scaling and bloating

In assigning grades to the different brands, allowances were made for differences in the severity of the test conditions as shown by the appearance of the check brand.

12. Expansion and Contraction The expansion and contraction of the bricks during a test was calculated from the measurements of length that were made before and after the test. The measurements are not of high accuracy but are sufficiently accurate to indicate any pronounced expansion or contraction. The per cent expansions of the check brand in the first six tests at Champaign were 0.43, 0.29, 0.15, 0.23, 0.36, 0.42, which are all of the same order of magnitude. The equivalent expansions and contractions of the other brands were calculated on a basis of 0.30% expansion of the check brand.

13. Other Calculations The data collected in these tests can also be used for calculating the effect of such defects as kiln marks on the probable life of a checker brick and the relation between the color of cross-section and the strength of a used brick. Microscopic and petrographic examination of the used brick should also yield interesting information.

IV. Laboratory Tests

14. Object of Laboratory Tests As a second step in the investigation, laboratory tests of checker brick have been undertaken with the object of finding what laboratory tests are of use for predicting the probable life of a checker brick in a carbureter and to point the way for the development of better checker brick. So far this work has been restricted to tests that could be made quickly.

15. Absorption The absorption of the new bricks was determined by the American Society of Testing Materials method for building brick (C21–20).

16. Compressive Strength The compressive strength of the new bricks was measured by the American Society of Testing Materials method (C21–20).

17. Permeability The permeability of each brand of brick, in terms of the volume of air (in cc) that will pass through the $2\frac{1}{2}$ inch thickness of the brick under one centimeter of water pressure, has been measured by means of a permeameter, designed for this purpose, which will be described in a forthcoming *Bulletin* of the University of Illinois Engineering Experiment Station.

18. Stoutness As in ordinary gas plant practice checker brick are subjected to a lot of rough handling; a number which roughly indicates a brick's ability to withstand rough handling is of significance. We obtain such a number by dividing the modulus of rupture of a brick by its weight, giving what we have called its "stoutness." That the values so assigned to the different brands have significance has been shown by our own experiences in handling the bricks. Bricks whose stoutness is less than 100 require care in handling.

19. Other Laboratory Tests Further laboratory tests including slag and spalling tests are planned.

Table II

Data Secured from Tests

	Laboratory tests						Tests 1–5 Champaign		
Brand	Weight (lbs.)	Transverse strength (lbs./sq.in.)	Compressive strength (lbs./sq. in.)	Stoutness	Permeability (cc/sec/cm.)	Absorption (%)	Equivalent decrease in strength (%)	Slagging and erosion	Equivalent change in length (%)
B	7.0	329	1200	47	7.2	11.7	59	C	0
C	7.7	1804	5000	234	0.64	6.4	91	A	0
D	7.1	576	2330	81	6.3	10.2	84	D	0
E	7.5	1245	3530	165	0.69	7.7	90	A	+0.3
F	7.0	433	1620	62	4.4	11.7	77	E	−0.6
G	7.4	957	3470	129	5.7	7.8	77	B	−0.14
H	7.3	1316	3740	180	1.4	7.5	80	A	0
I	7.0	727	2100	104	3.0	10.1	79	B	−0.34
J	7.6	1478	4980	194	0.49	7.4	87	A	+0.18
K	6.6	843	2710	128	0.38	18.0	92	B	+1.3
L	6.9	426	2030	62	2.1	11.4	68	B	+0.5

V. Preliminary Data from Tests

20. Summary of Data Table II gives a summary of the data which have been secured from the first five commercial tests in Champaign and from laboratory tests of the eleven brands included in these tests. The data pertaining to these brands which was furnished by the manufacturer is given in Table I (Par. 5). This data is presented at this time to help in promoting discussion and criticism of the methods of conducting these tests which have been described above. Until more tests have been completed and the data from Chicago is compared with that from Champaign, it is not advisable to draw any conclusions.

VI. Summary

A progress report of an investigation of checker brick for carbureters which is being conducted by the Department of Ceramic Engineering of the University of Illinois in coöperation with the gas companies of northern Illinois has been presented. The methods used in carrying out commercial and laboratory tests and the data so far obtained have been submitted for discussion and criticism. When the investigation has been completed a final report will be made.

THE DETERMINATION OF THE BULK AND PORE VOLUMES OF REFRACTORY MATERIALS[1]

By M. L. Hartmann[2], O. B. Westmont[3] and S. F. Morgan[3]

ABSTRACT

A new sand displacement method for the determination of the bulk volume and bulk specific gravity of refractory or other material is described.

A gas porosimeter with a vertical U-tube manometer for the determination of pore volumes of materials is also described together with calculations of the possible errors.

The porosities, bulk specific gravities, and calculated true specific gravities of 15 types of refractory bricks obtained by means of these two methods, and the usual water absorption method are tabulated for comparison.

The resistance of the refractory structures to slag penetration, to spalling, to heat conduction, etc., is not only related to the composition but also to a great extent to the porosity of the materials used. The relationship of these factors to the pore space in refractories has been emphasized by many recent investigators. An accurate and convenient method for determining the percentage of pores in these materials is therefore of considerable interest.

The usual method for determining the pore space in refractory and other ceramic materials is that of liquid absorption. It was, however, found by Washburn and Bunting[4] that this method was not reliable in that the complete filling of all the pores of many bodies was not possible in a reasonable length of time. In their work the gas expansion method was developed and later modified by Bole and Jackson.[5] The principle of this method is to allow the gas which occupies the pores of the specimen to expand into an evacuated chamber of known volume and to measure the resulting change in pressure.

In the apparatus described by Bole and Jackson, an inclined gage with a large mercury reservoir was used for measuring this change in pressure. A similar inclined gage (ratio 7 to 1), using both a 2 mm. and a 4 mm. inside diameter tube, was constructed for our tests and found to be impracticable. In order to obtain constant pressure readings with the sluggish mercury column, the tube required excessive tapping to bring it to true equilibrium.

The apparatus described by Pressler[6] for standard brick was the same general type as that of Bole and Jackson, except that a vertical tube was used. Both of these methods require a large amount of mercury

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[4] E. W. Washburn and E. N. Bunting, *Jour. Amer. Ceram. Soc.*, **5**, 112 (1922).

[5] G. A. Bole and F. G. Jackson, *Brick and Clay Rec.*, **61** [5], 314 (1922).

[6] E. E. Pressler, *Jour. Amer. Ceram. Soc.*, **7**, 154 (1924).

which must be maintained at a certain level in order to prevent errors in the calculations of all pressures. This mercury must also be cleaned frequently.

In our final work an open end vertical manometer similar to the one shown by Washburn and Bunting (general method) was used. With this type of manometer (6 mm. bore) no reservoir of mercury is required and only very slight tapping is necessary to obtain a constant pressure reading.

In all the previous work on the determination of the porosity of ceramic bodies, the bulk volume was determined either by direct measurement or by liquid displacement after the surface pores had been sealed. By direct measurement only bodies having very regular shapes can be selected for test, and by liquid displacement considerable trouble is encountered in thoroughly coating the surfaces without changing the true bulk volume. The precision with which the porosity of a specimen can be determined is limited by the accuracy of the bulk volume measurement.

In making our porosity tests the bulk volumes are all measured by sand displacement. By this method the difference in volume of sand displaced by the specimen and a metallic standard of approximately the same size and shape is determined and the bulk volume of the specimen calculated.

The bulk and pore volume determinations will be described separately.

I. Bulk Volume

A. Apparatus For the measurement of the bulk volume the apparatus shown in Fig. 1 is used. This apparatus consists of a rigid hopper fitted with a quick opening slide at the bottom for delivering the sand to the wooden box containing the test specimen. The hopper is supported over a funnel-shaped tray, which directs the overflow of grain into a receiver.

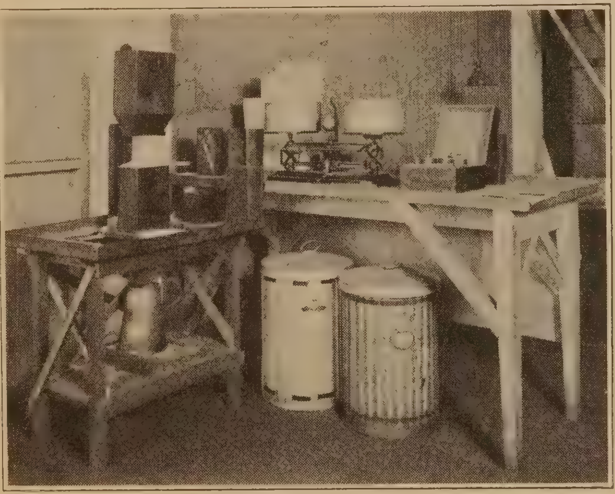

FIG. 1.

The sand used is especially graded zircon grain (through 124- on 148-mesh). The metallic standards corresponding approximately to the sizes of the specimens tested are accurately machined steel blocks. The wooden containers are shellaced oak boxes with mortised joints.

B. Procedure In determining the bulk volume of a specimen a thin layer of sand, about ¼ inch deep, is poured into the wooden container. The metallic standard is placed centrally in the box, which is then set directly under the hopper orifice. The slide is pulled quickly, allowing the sand to fill the box and overflow. The excess is carefully scraped from the top of the box with a straight edge.

The weight of the annular sand is recorded and the operation repeated using the sample instead of the standard. The difference in the two weights thus obtained divided by the bulk specific gravity of the sand is equal to the difference in volumes of the standard and specimen.

C. Calculations The weight of the sand around the standard divided by the calculated annular volume is equal to the bulk specific gravity of the sand. The annular volume is the difference between the volume of the box and the standard. The bulk volume of the specimen is calculated by the formula:

$$V_t = V_s \pm \frac{W}{D}$$

where V_t = bulk volume of specimen
V_s = volume of standard
W = difference in weight of annular sand around standard and specimen
D = determined bulk specific gravity of zircon sand

D. Discussion of Methods Zircon sand was selected in preference to other granular materials since it consists of hard, rounded, and very uniform particles. It also has a high specific gravity so it flows freely and readily fills all the cavities in irregular specimens. The sand does not break down appreciably even after a long series of tests.

In using this sand method the most accurate data is obtained when the standard and the specimen are identical in size and shape. The packing of the sand is then the same in both cases. In determining the bulk volume of refractory brick the standard is 9x4½x2½ inches so that the difference in its volume and that of the specimen is very small. The box used is 10x6x4 inches. With this box the annular space is not excessive and yet it is large enough to allow the sand to flow freely on all sides of the sample.

Since the difference in bulk volume of the standard and the sample is only a small percentage of the total volume, it is evident that the volume of the specimen can be determined to the same precision as it is possible to measure the metal standard.

The weight of the annular sand can be duplicated practically to the same precision as it is possible to weigh. As the result of two hundred (200) weighings of annular sand around full size bricks (1650 cc.) it was determined that the annular sand weight is accurate to within one gram. (Weight of annular sand equals 5500 grams; bulk specific gravity of sand, 2.60). The error in duplicating bulk volume measurements of a standard size brick is less than .06%. Since the total volume of a standard size brick is comparatively large, the surface pores have little effect in the determination of the bulk volume.

II. Pore Volume

A. Apparatus The gas expansion method for determining pore volume is shown in Fig. 2. The number of containers and expansion bottles depends upon the variation in the sizes of the samples and the accuracy desired. The glass expansion bottles may be omitted if desired and the containers may be used as expansion chambers. It is easier, however, to trace and eliminate air leaks if glass bottles are used for the expansion chambers.

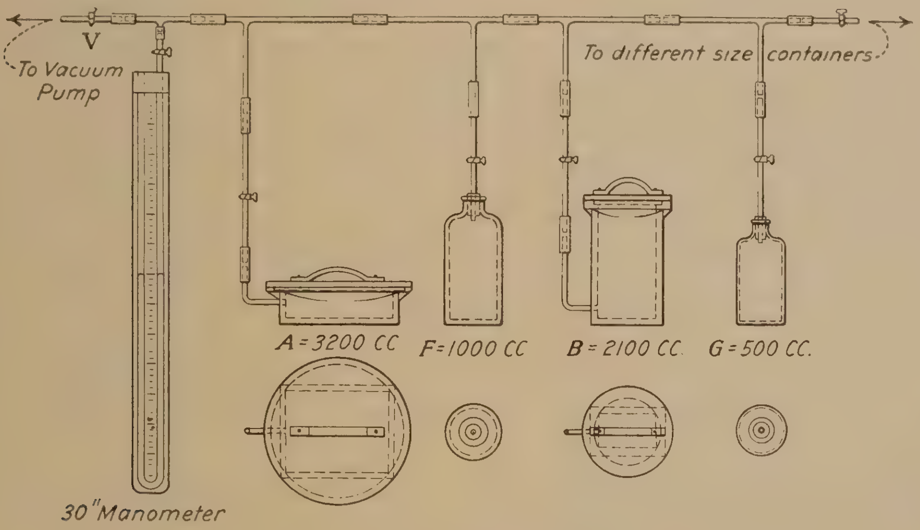

FIG. 2.—Gas porosimeter.

The containers are made of one-half inch cast iron. The covers are ground to fit and are greased to assure air-tight joints. The outside of each container is painted with several coats of shellac to prevent air leaking through the castings.

The containers are designed to accommodate refractory tile and standard bricks. They are made with approximately $\frac{1}{8}$ inch clearance on all sides of the specimen to be tested. The volume of each of the containers is made adjustable by the addition of shims and plates of steel so that they can be used with smaller specimens. The maximum precision is attained when the free space around the specimen is reduced to a minimum.

The expansion chambers consist of different size glass bottles. The heavy rubber connections to the bottles are coated with shellac.

Three-way glass stopcocks are used to connect the iron containers to the vacuum tube. Mercury sealed stopcocks are used in connections to the glass bottles.

The pressure gage is a vertical mercury manometer with one end of the U-tube opened to the air. The scale is of tempered steel and is calibrated in hundredths of an inch. By the aid of the magnifying glass, the scale is read to the nearest .001 inch. Two-mm. tubing is used throughout in order to reduce the volume of the connectors.

B. Procedure

The sample to be tested is placed in the most suitable container. Shims and plates of steel are added to the container to reduce the free space. The cover is placed on the container and the three-way stopcocks are turned so as to open all the containers to the atmosphere.

A rough estimate is made of the volume of the free space plus the pore volume of the specimen. Then the bottle or combination of bottles whose volume approaches this estimated volume is decided upon, and the mercury sealed stopcocks are turned so as to throw these selected bottles into the vacuum line.

Stopcock V is opened and the selected expansion bottles are evacuated to about twenty-eight inches of mercury. When this vacuum is obtained, stopcock V is closed and the height of the mercury is read (P_1). Then the stopcock of the container in which the sample is held is turned so as to allow the enclosed air to expand into the evacuated expansion bottles. When the mercury has reached a constant value (after about twenty-five seconds) the height of the mercury above zero is read (P_2). The vacuum is then released and the test repeated for check readings.

The sample is removed from the containers and the same procedure is followed to determine the volume of the container minus the shims and plates used.

C. Calculations

NOTATIONS

P_A = atmospheric pressure.
P_B = pressure existing in evacuated expansion bottles.
P_1 = gage reading corresponding to P_B.
P_E = pressure existing in system after air in container has expanded into bottles.
P_2 = gage reading corresponding to P_E.
V_B = volume of expansion bottles used plus all connecting tubing, including the manometer tube as far as the first reading P_1.
V_C = unknown volume of container minus shims and plates used, plus tubing to three-way stopcock.
V_{C1} = unknown volume of free space in container plus pore volume, plus tubing to three-way stopcock.
V_E = volume of mercury gage between P_1 and P_2.

(1) $P_B V_B + P_A V_C = P_E(V_B + V_C + V_E)$ (Temperature constant).

Only one reading is necessary to determine each pressure. The height of the mercury above the zero level is read. The difference in the atmospheric pressure and the pressure within the system is equal to twice the reading plus the correction factor (ΔP) which must be added due to the irregularity of the bore of the tube. The true pressures

$$P_B = P_A - (2P_1 + \Delta P_1)$$

$$P_E = P_A - (2P_2 + \Delta P_2)$$

$$(2) \quad [P_A - (2P_1 + \Delta P_1)]V_B + P_A V_C = [P_A - (2P_2 + \Delta P_2)](V_B + V_C + V_E)$$

$$(3) \quad V_C = V_B \frac{(P_1 + \frac{1}{2}\Delta P_1)}{(P_2 + \frac{1}{2}\Delta P_2)} - V_B + V_E \frac{[P_A - (2P_2 + \Delta P_2)]}{(2P_2 + \Delta P_2)}$$

$$V_E = \pi r^2 (P_1 - P_2) 2.54$$

r = radius of tube = .29 cm.

$$V_E = .67 (P_1 - P_2)$$

$$(4) \quad V_C = V_B \frac{(P_1 + \frac{1}{2}\Delta P_1)}{(P_2 + \frac{1}{2}\Delta P_2)} - V_B + .67\,(P_1 - P_2) \frac{[P_A - (2P_2 + \Delta P_2)]}{(2P_2 + \Delta P_2)}$$

Since the third term in equation (4) is usually a very small part of the entire volume and is only ever determined to two significant figures, a curve is plotted assuming P_A and P_1 constant. Then the value of the third term is found by merely reading from the curve (Fig. 3), the value that corresponds to P_2.

A curve (Fig. 4) is also plotted to show the relationship of the manometer bore correction factor ($\frac{1}{2}\Delta P$) to P.

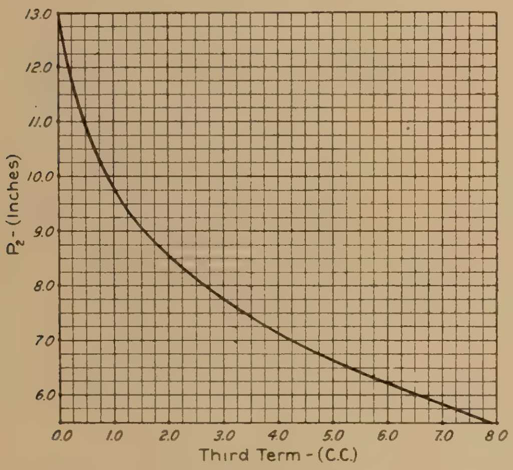

FIG. 3.—Evaluation of third term (Section II C, Equation 4).

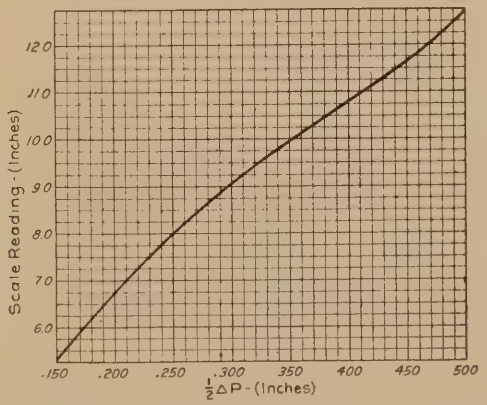

FIG. 4.—Calibration curve for manometer.

Similar calculations are made to determine V_{C_1}.

$V_o = V_c - V_{c1}$ = volume of solid portion of sample.

$$\text{Per cent porosity} = 100 \frac{(V_t - V_o)}{V_t}$$

where V_t is the bulk volume.

D. Discussion of Method

In the above calculations it will be noted that the comparatively large manometer tube does not introduce an error in the results since its volume and that of all the connections are taken into consideration. The tube is also calibrated so that no errors result from irregularities in the bore. With this calibration rapid determination can be made since only one mercury level need be read.

The error in the measurement of volumes resulting from an error of .001 inch in reading P_1 and also P_2 depends upon the relation between the volume of the expansion chamber and the volume of gas in the container.

The approximate formula for calculating V_C is

(1) $$V_C = V_B \frac{(P_1 - 1)}{P_2}$$

The deviation in V_C caused by an error of .001 inch $= \partial P_1$, in measuring P_1 is

$$\Delta_1 = \frac{V_B \partial P_1}{P_2} = .001 \frac{V_B}{P_2}$$

The deviation in V_C caused by an error of .001 inch $= \partial P_2$, in measuring P_2 is

$$\Delta_2 = -V_B \frac{P_1 \partial P_2}{P_2^2} = -.001 \frac{V_B P_1}{P_2^2}$$

The combined effect is

(2) $$\Delta = \sqrt{\Delta_1^2 + \Delta_2^2} = \frac{.001\, V_B}{P_2} \sqrt{1 + \frac{P_1^2}{P_2^2}}$$

Let x = ratio of expansion chamber volume to gaseous volume in the container. Then

(3) $$V_B = x V_C$$

(4) Substituting in equation 1.

$$\frac{P_1}{P_2} - 1 = \frac{1}{x}$$

(5) Substituting in equation 2.

$$\Delta = \frac{.001\, V_C}{P_1} (1+x) \sqrt{1 + \frac{(1+x)^2}{x^2}}$$

$$\text{Per cent error } = \frac{\Delta 100}{V_C} = \frac{.001}{P_1} (100)(1+x) \sqrt{1 + \frac{(1+x)^2}{x^2}}$$

Let P_1 be about 14.0 inches.

$$\text{Then, per cent error } = (100)\frac{.001}{14} (1+x) \sqrt{1 + \frac{(1+x)^2}{x^2}}$$

The following table is calculated from this formula.

From Table I it can be seen that the error due to reading the scale is very small if the ratio of the volume of the expansion chamber and gaseous volume of the container is near unity.

In the case of the full size bricks tested the error in measuring the volume of the solid portion of the brick amounts to less than 1 cc.

The error in measuring the total volume is also less than 1 cc. Therefore, the combined error in determining the porosity of a brick amounts to considerably less than .1%.

TABLE I

When x =	$\frac{1}{10}$	$\frac{1}{5}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{2}$	1	2	3	4	5	10	100
Error	%	%	%	%	%	%	%	%	%	%	%	%
(Vol.)	.085	.050	.045	.040	.035	.020	.040	.045	.055	.065	.12	1.0
Examples if volume is	cc	cc	cc	cc	cc	cc	cc	cc	cc	cc	cc	cc
100 cc	.09	.05	.05	.04	.04	.02	.04	.05	.06	.07	.12	1.0
200 cc	.17	.10	.09	.08	.07	.04	.08	.09	.11	.13	.24	2.0
1000 cc	.9	.5	.5	.4	.4	.2	.4	.5	.6	.7	1.2	10.0
2000 cc	1.7	1.0	.9	.8	.7	.4	.8	.9	1.1	1.3	2.4	20.0
4000 cc	3.4	2.0	1.8	1.6	1.4	.8	1.6	1.8	2.2	2.6	4.8	40.0

III. Comparative Porosity Tests on Different Types of Refractories

In order to compare the data obtained by the above described method to that obtained by the usual water absorption method, several tests were made on different types of standard refractory bricks having a wide range in porosity.

The samples used for the gas expansion tests were all 9x4½x2½ inches, while those used for water absorption were 4½x2½x2½ inches. In Table II shown above, the data (*a*) and (*b*) were secured from sections cut from opposite ends of the brick on which the gas porosities were measured. It will be noted that in several cases under the water method that check values are recorded. In all the check tests the specimen on which the first value was determined was oven dried at 150°C for 36 hours and allowed to cool in the air before the second test was made.

In the water absorption method the specimen was first oven-dried and weighed. It was then boiled for four hours in a container into which steam was continually fed. After cooling in water to room temperature the suspended and wet weights were determined. In obtaining the wet weight the sample was removed from the water and allowed to drip for a few seconds with the 4½x2½-inch surface in a horizontal position until a single drop adhered to the center of the flat surface before the piece was placed in the balance pan.

In securing the wet weight of a porous body, it is evident that there may be considerable water removed from the surface pores. It is,

TABLE II

EXPERIMENTAL RESULTS

Refractory material	Per cent porosity			Bulk specific gravity			Calcd. true sp. gr		
	Gas method	Water method (*a*)	Water method (*b*)	Gas method	Water method (*a*)	Water method (*b*)	Gas method	Water method (*a*)	Water method (*b*)
Carborundum No. 1	37.0	35.2		2.06	2.06		3.26	3.18	
		36.3	35.7		2.06	2.04		3.24	3.18
	35.5	34.4		2.10	2.10		3.25	3.20	
		35.1	34.2		2.09	2.08		3.22	3.16
	36.6	34.7		2.08			3.25	3.16	
	36.2	34.9		2.06			3.24	3.18	
Carborundum No. 2	19.4	16.4	16.2	2.53	2.56	2.56	3.13	3.06	3.06
	21.7			2.43			3.09		
	21.6	17.9	17.1	2.43	2.42	2.45	3.12	2.95	2.96
	21.4	19.5	17.8	2.43	2.41	2.46	3.09	3.00	3.00
		20.0			2.41			3.01	
Fused Alumina No. 1	20.3	20.3		2.84	2.84		3.56	3.56	
	19.8	20.2		2.84	2.83		3.55	3.55	
	20.4	20.3		2.82	2.84		3.55	3.56	
	21.9			2.78			3.56		
Fused Alumina No. 2	22.1	22.9	22.3	2.76	2.72	2.75	3.53	3.53	3.54
	21.4	22.2	21.4	2.79	2.76	2.78	3.56	3.55	3.54
	22.3	22.3		2.76	2.75		3.55	3.54	
	22.3	22.5		2.76	2.74		3.54	3.54	
Fused Alumina No. 3	18.4	19.0		2.99	2.97		3.66	3.66	
	18.3	18.5		2.98	2.98		3.65	3.66	
	18.6	18.5		2.97	2.96		3.65	3.66	
	18.6			2.98			3.65		
High Alumina No. 1	31.2			2.01			2.93		
	29.1	28.0	26.9	2.04	2.04	2.06	2.88	2.84	2.82
	32.1	31.0		1.99	1.99		2.93	2.88	
	29.1	28.2		2.04	2.03		2.88	2.83	
High Alumina No. 2	32.9	31.1		2.02	2.04		3.02	3.01	
		32.2			2.04			3.01	
	29.6	27.8	27.5	2.12	2.19	2.17	3.01	3.03	3.00
		27.2	27.0		2.18	2.18		3.00	3.00
	31.6	32.7		2.05	2.01		3.00	3.01	
		32.8			2.02			3.00	
High Alumina No. 3	39.6	40.1	39.6	1.84	1.81	1.83	3.06	3.03	3.05
		41.3	39.2		1.79	1.84		3.05	3.05
	39.6	40.0		1.84	1.81		3.06	3.02	
		40.5			1.81			3.05	
	39.0	39.1		1.86	1.85		3.06	3.05	
		38.5			1.86			3.04	
	39.6	39.8		1.85	1.82		3.06	3.03	
		39.4			1.84			3.05	

TABLE II (*concluded*)

Refractory material	Per cent porosity			Bulk specific gravity			Calcd. true sp. gr.		
	Gas Method	Water method (*a*)	(*b*)	Gas method	Water method (*a*)	(*b*)	Gas method	Water method (*a*)	(*b*)
High Alumina No. 4	39.6	40.5		1.88	1.83		3.11	3.08	
		40.8			1.83			3.10	
	40.7	40.6		1.85	1.83		3.12	3.08	
		41.0			1.83			3.10	
	39.4	37.8		1.88	1.91		3.12	3.08	
		37.9			1.91			3.08	
	39.4	37.9		1.89	1.91		3.12	3.08	
		37.6			1.92			3.08	
Kaolin Brick	32.4	31.8		1.88	1.87		2.77	2.75	
	32.8			1.87			2.77		
First Quality Fire Clay	24.2	24.4	23.3	2.05	2.04	2.07	2.70	2.70	2.70
		25.1	23.3		2.03	2.07		2.71	2.70
	23.0	22.6		2.08	2.08		2.70	2.70	
		23.3			2.07			2.70	
	24.3	24.5		2.04	2.02		2.69	2.60	
		24.3			2.03			2.68	
	22.7	23.6		2.08	2.06		2.70	2.70	
		22.9			2.08			2.70	
	25.4			2.02			2.70		
Fireclay Insulating Brick	47.6	47.5		1.45	1.47		2.77	2.79	
	43.7			1.57			2.77		
	44.5			1.53			2.76		
	45.0	44.8		1.51	1.52		2.76	2.76	
High Temperature Insulating Brick	68.9	68.0		.879	.880		2.83	2.78	
	68.6			.885			2.83		
	72.9	72.3		.764	.760		2.83	2.81	
	72.9			.764			2.82		
Low Temperature Insulating Brick No. 1	72.9	72.9		.650	.640		2.40	2.36	
	72.5	71.0	72.5	.660	.680	.647	2.40	2.35	2.35
		71.4			.676			2.36	
	72.9	72.9		.651	.636		2.40	2.35	
	73.3			.647			2.40		
Low Temperature Insulating Brick No. 2	82.0	81.7		.459	.456		2.55	2.50	
	81.3	80.9		.479	.480		2.55	2.51	
	81.1			.470			2.50		
	81.6			.455			2.50		

however, believed that by this method the excess of water on the lower surface of the sample is approximately the same as that which runs from the pores on the upper surfaces so that the wet weight is more accurate than if the specimen were dried with a damp cloth. The data shown above for the water method were all determined by the same operator so the results are comparable.

Kind of Refractories Tested

The carborundum brick No. 1 were made entirely of carborundum and were recrystallized in an electric furnace. The carborundum brick No. 2 were ceramically bonded and kiln fired at 1350°C. The fused alumina brick Nos. 1, 2, and 3 were all bonded with approximately 20% of raw clay and fired at 1350°C. The high alumina refractories Nos. 1 and 2 were fairly strong and dense. No. 2 was kiln fired to cone 19 (1510°C). The high alumina bricks Nos. 3 and 4 were quite coarse and open. They were fired to cone 15 (1430°C). The kaolin brick were fairly dense and were fired to cone 15.

The first quality fireclay samples were dense commercial fire brick. The fireclay insulating brick were fairly porous and were high fired. The high temperature insulating refractories were very porous and had been fired to high temperatures. The low temperature insulating refractories Nos. 1 and 2 were commercial bricks containing diatomaceous earth.

Example of Calculations

Carborundum Brick No. 1B.

(1) Determination of bulk volume (by sand displacement method)

Volume of density box = 3791 cc.
Volume of metallic standard brick = 1658 cc.
Volume of annular sand = 3791 − 1658 = 2133 cc.
Weight of annular sand around std. brick = 5540 gms.

$$\text{Bulk specific gravity of sand} = \frac{5540}{2133} = 2.60 \text{ gms/cc.}$$

Algebraic difference in weights of annular sand around standard and brick = +40 gms.
Check = +40 gms.

$$\text{Bulk volume of brick} = 1658 + \frac{40}{2.60} = 1673 \text{ cc.}$$

(2) Determination of pore volume (by gas expansion method)

	Check Readings
$P_1 = 12.960$	$P_1 = 12.960$
$P_2 = 7.658$	$P_2 = 7.658$

Volume of expansion bottle = 1445 cc.
From calibration chart (Fig. 4)

$\frac{1}{2}\Delta P_1 = +.492$
$\frac{1}{2}\Delta P_2 = +.216$

From valuation chart (Fig. 3) the effect of third term = 3 cc.

$$V_{c1} = V_B \frac{(P_1 + \frac{1}{2}\Delta P_1)}{(P_2 + \frac{1}{2}\Delta P_2)} - V_B + .67(P_1 - P_2)\,\frac{[(P_A - (2P_2 + \Delta P_2))]}{(2P_2 + \Delta P_2)}$$

$$V_{c1} = 1445 \frac{(12.960 + .492)}{(7.658 + .216)} - 1445 + 3 = 1029 \text{ cc.}$$

Likewise the volume of the container is calculated.

$V_c = 2108$ cc.

$$\text{Per cent porosity} = 100\,\frac{[V_t-(V_c-V_{c1})]}{V_t} = 100\,\frac{[1673-(2108-1029)]}{1673} = 35.5$$

(3) Bulk specific gravity (by sand displacement method)

$$\frac{\text{Dry weight}}{\text{Total volume}} = \frac{3505}{1673} = 2.095$$

(4) Calculated true specific gravity (by gas expansion method)

$$\frac{\text{Dry weight}}{\text{Volume of solid portion of brick}} = \frac{3505}{(2108-1029)} = 3.25$$

(5) Determination of porosity (by water method)

Dry weight = 741.9 gms.
Wet weight = 866.5 gms.
Suspended weight = 511.6 gms.
Pore water = wet weight − dry weight
= 866.5 − 741.9 = 124.6 gms.
Bulk volume = wet weight − suspended weight
= 866.5 − 511.6 = 354.9

$$\text{Per cent porosity} = \frac{\text{Pore water (100)}}{\text{Bulk volume}} = \frac{124.6\,(100)}{354.9} = 35.1$$

(6) Bulk specific gravity (by water method)

$$\frac{\text{Dry weight}}{\text{Bulk volume}} = \frac{741.9}{354.9} = 2.090$$

(7) Calculated true specific gravity (by water method)

$$\frac{\text{Bulk specific gravity (100)}}{100-\text{per cent porosity}} = 3.22$$

Time Required to Make Determinations

The total time required to make a routine porosity determination is approximately twelve minutes. The bulk volume determination by the sand displacement method requires about three minutes. This average time is reduced considerably when several tests are made and the bulk specific gravity of the sand is only determined once for the lot. The pore volume is measured and checked in about four minutes, and the calculations made in five minutes.

Discussion of Results

It will be noted from the above results that with the carborundum refractories the gas expansion porosities are 1 to 3% higher than the water absorption values. This is probably due to the fact that the air diffuses through pores into which water cannot penetrate.

The porosities of the fused alumina bricks obtained by both methods check very closely. All the values on the fireclay brick check within approximately 1%. It is, of course, realized that there may be a variation of over 1% in the porosity in different sections of a given brick as shown by the data listed under (*a*) and (*b*). Some difference in gas porosity on the whole brick and the water porosity on about $\frac{1}{4}$ of the same brick is, therefore, due to variations in the material itself.

The results on the very porous insulating refractories obtained by the two methods check very closely. In these bricks the number of sealed pores is probably very small.

The specific gravities calculated from the gas porosity results are almost identical for a given lot of bricks, while those calculated from the water porosities show considerable variation.

All the porosity data recorded under the gas expansion method could be calculated to four significant figures. This, however, would involve unnecessary work since at present bricks made from the same mix and fired in the same kiln differ in porosity by more than 1%.

Conclusions

1. The rapid determination of the bulk volume of refractory or other ceramic materials can be made by the use of a new sand displacement method.

2. The error in measuring this volume of standard brick is less than 0.06%.

3. An accurate measurement of the pore volume of materials can be made by the use of a gas expansion apparatus fitted with an open end U-tube manometer.

4. In using these two methods the error in determining the porosity of refractory brick is less than 0.1%.

5. Comparative tests by the use of these two methods and the water absorption method show (1) very close results (generally within 1%) with thirteen types of refractory materials, and (2) slightly low water porosities with two types of carborundum materials.

Note: Acknowledgment is made in particular to G. H. Porter of this Laboratory for his original suggestion to use sand displacement for bulk volume.

THE MERCURY BALANCE—AN APPARATUS FOR MEASURING THE BULK VOLUME OF BRICK[1]

By A. E. R. Westman[2]

ABSTRACT

A new apparatus for measuring the bulk volume of bricks, called the mercury balance, has been described and its method of operation given in detail. Its great accuracy and other advantages would recommend its use when a large number of very accurate measurements of bulk volume are required.

I. Introduction

1. Definition of Bulk Volume

A brick contains solid material, open pores, and closed pores. In describing a brick, the three terms "true volume," "apparent volume," and "bulk volume" are used. The true volume of a brick is the volume of the solid material only, the apparent volume is equal to the sum of the true volume and the volume of the closed pores, and the bulk volume is equal to the sum of the apparent volume and the volume of the open pores. The bulk volume of a brick is thus the over-all volume, or what would ordinarily be meant by the term "volume" without any qualifications.

2. Importance of Bulk Volume Measurements

It is frequently necessary in the investigation of the properties of fire brick and similar ceramic products to make accurate determinations of the bulk volume of a number of bricks. Such measurements are, for example, of great use in determining accuracy of molding, in calculating the porosity from a knowledge of the pore volume and especially in determining the small changes in volume that occur in permanent expansion and contraction tests. It is therefore a great convenience to have a simple, accurate and rapid method for determining the bulk volume of bricks.

II. Present Methods of Measuring Bulk Volume

3. The Work of Previous Investigators

Schurecht,[3] Shaw,[4] Staley,[5] Spurrier[6] and Goodner[7] have developed volumeters of different types for measuring the bulk volumes of small briquets. Goodner reviews and criticizes the methods which require a preliminary soaking of the briquet in some liquid. None of the methods which have been developed for measuring briquets can be used conveniently for measuring standard brick. The methods which are used for measuring standard brick at the present time will be briefly reviewed here.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division). Recd. Dec. 14, 1925.

[2] Research Associate in Ceramics, Engineering Experiment Station, University of Illinois, Urbana, Ill.

[3] *Jour. Amer. Ceram. Soc.*, **1**, 556 (1918); *Ibid.*, **3**, 730 (1920).

[4] *Jour. Amer. Ceram. Soc.*, **2**, 480 (1919).

[5] U. S. Bur. of Stand. Rept., "Construction and Tests of Staley Volumeter," Verbal Request of Committee of Standards of the Amer. Ceram. Soc., Feb., 5 (1919).

[6] *Jour. Amer. Ceram. Soc.*, **3**, 400 (1920).

[7] *Jour. Amer. Ceram. Soc.*, **4**, 288 (1921).

4. The Caliper Method In the caliper method the volume of a brick is calculated from the average linear dimensions of the brick which are obtained by making several caliper measurements of each dimension. With well-shaped bricks the bulk volume can be determined to within 1% by this method if care is taken. If the shape of the brick departs materially from that of a true rectangular parallelopiped or has broken edges this method is uncertain.

5. The Immersion Method[1] This is the most accurate method in common use.[1] The brick is soaked and then weighed in kerosene, or some similar liquid, giving what is called the "suspended weight." It is then removed from the liquid, wiped with a moist cloth and weighed in air giving the "wet weight." The bulk volume of the brick is then obtained by dividing the difference between the wet and suspended weights by the density of the liquid used. In cases where some liquid other than water must be used the temperature of the liquid must be very accurately controlled. In either case it often happens that the liquid soaked up by the brick must be removed before further tests can be carried out; this involves a subsequent drying or firing which not only entails a loss of time, but may affect the properties of the brick. For this reason this method is inconvenient for permanent expansion or contraction tests.

6. The Air Expansion Methods In this method the brick is coated with a sufficiently thick layer of beeswax to hold a partial vacuum and the volume obtained by means of an air expansion porosimeter.[2] This method is not as accurate as other methods and the trouble and loss of time involved in removing the wax coating precludes its use except in connection with porosity measurements by the air expansion method.

7. The Displacement Method In the displacement method the brick is placed in a container whose volume is known and the volume of the brick calculated from the volume of liquid necessary to fill the remaining space in the container. If kerosene is used the brick must be soaked to saturation before being measured, but if mercury is used this is not necessary. This method and its modifications are very useful for measuring small briquets, but in order to secure sufficient accuracy when standard bricks are measured, a clamped cover and gasket are necessary and this introduces uncertainties. Attempts have been made to use zircon grain instead of mercury but, as the zircon grain did not pack to the same extent in every measurement, only approximate results could be secured.[1]

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[1] American Society of Testing Materials, Standard C 20–20, p. 742 (1924).

[2] E. E. Pressler, *Jour. Amer. Ceram. Soc.*, **7** [3], 154–59 (1924).

III. The Mercury Balance

8. The Operating Principle of the Mercury Balance

A new apparatus, which we have called the mercury balance, has been developed in this laboratory during the past year and has been found to be very convenient for measuring the bulk volume of fire brick. It lends itself readily to such extreme accuracy that it should prove useful in many investigations. The mercury balance operates on the principle that a brick, when immersed in mercury, displaces a volume of mercury equal to its bulk volume and that the mercury exerts an upward thrust on the brick which is equal to this volume multiplied by the density of the mercury. In the mercury balance the upward thrust of the mercury is measured by finding the weight necessary to balance it and from a knowledge of the density of the mercury the bulk volume can be calculated. The arrangement of the balance is such that the center of gravity of the moving system is situated about eighteen inches below the position of the brick being measured, which stabilizes the moving system as a whole and keeps the brick in in a horizontal position; thus no difficulty is encountered from using a heavy liquid like mercury for the immersion medium.

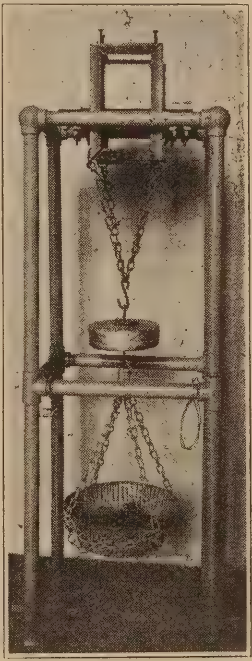

FIG. 1.—The mercury balance.

IV. Description of the Mercury Balance

9. General Description

A picture and a diagram of the mercury balance, which is used for measuring the bulk volume of standard straight bricks (9x4.5x2.5 inches), are shown in Figs. 1 and 2 respectively. It is used in conjunction with a torsion balance that will weigh 4 kilograms to 0.5 grams and consists of a mercury trough, a saddle, a permanent weight, a scale pan and a supporting framework.

10. The Mercury Trough

The mercury trough (1, Fig. 2) is a cast iron box with walls $\frac{3}{8}$ inch thick and inside dimensions 10x$5\frac{1}{2}$x$5\frac{5}{8}$ inches. It is bolted to two $\frac{1}{2}$x2-inch steel straps which are in turn bolted to an iron pipe framework 4 feet

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[2] Since this paper was written, the author has learned that Hartman, Westmont, and Morgan, *This Jour.*, pp. 298-310, have made accurate bulk volume measurements with zircon grain by using a comparative method.

high. A pet-cock is used for adjusting the mercury level and for removing the mercury for cleaning.

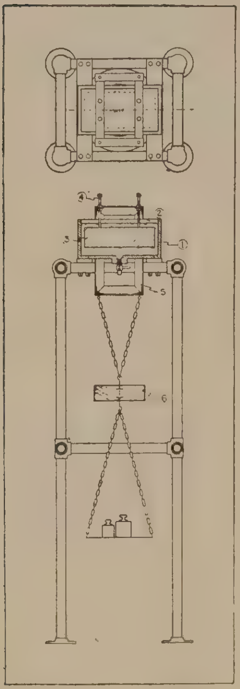

Fig. 2.—The mercury balance.

11. The Saddle The saddle (5, Fig. 2) was made from pieces of 1x1 inch angle iron which were rivetted together so as to form a rectangular cage $9\frac{3}{4} \times 9\frac{1}{2} \times 6\frac{1}{4}$ inches. Four $4 \times \frac{1}{4}$-inch bolts are fastened to it by means of lock nuts at points situated at the corners of a rectangle $5 \times 2\frac{1}{2}$ inches. Marks were made at exactly $\frac{1}{2}$ inch from the lower ends of the bolts and the combined volume of these $\frac{1}{2}$-inch lengths so marked off was calculated from their dimensions and found to be 0.75 cc.

12. The Permanent Weight The permanent weight (6, Fig. 2) was cast from babbitt and its weight adjusted until the weight of the moving system consisting of saddle, permanent weight, scale pan, and suspending chains was 14,000 grams, which was just insufficient to cause the smallest and heaviest brick we were to measure to sink in mercury. The permanent weight was suspended from the saddle by means of steel chains.

13. The Scale Pan The scale pan (Fig. 1) was suspended from the permanent weight by means of chains and consisted of an ordinary graniteware pan.

V. Operation of the Mercury Balance

14. Leveling About three inches of mercury is put in the trough (1, Fig. 2) and the brick to be measured is slipped under the saddle (5, Fig. 2), from which the permanent weight and scale pan have been removed, and adjusted to such a position that it floats in a horizontal position on the mercury, the edge of the trough serving as a level edge for comparison.

15. Balancing The permanent weight and scale pan are then hung on the saddle; sufficient weights to make the brick sink to the bottom of the trough are added to the scale pan and the mercury level adjusted until there is at least $1\frac{1}{2}$ inches of mercury above the brick. The weights in the scale pan are then varied until a balance is secured and the brick remains stationary in such a position that the marks on the bolts[1] are just level with the surface of the mercury, and the value of this balancing weight is noted. When a balance is secured, there will be $\frac{1}{2}$ inch of mercury above and 1 inch of mercury below the brick; in this position surface tension effects are negligible although they are quite marked when the brick comes within $\frac{1}{8}$ inch of the top or bottom surface of the mercury.

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[1] See §§11, above.

16. Measuring Temperature The temperature of the mercury is measured to within 0.25°C by means of a thermometer and the corresponding density found from temperature-density tables, which are given in most handbooks.

17. Weighing and Calculating The brick is now removed from the balance, brushed off and weighed on a torsion balance to 0.5 grams. To this weight is added the combined weights of the moving system (14,000 grams) and the balancing weight[1]; the sum, so obtained, is then divided by the density of the mercury giving the volume of the mercury displaced. The volume of the parts of the bolts that were immersed in the mercury (0.75 cc) is subtracted from this volume and the bulk volume of the brick obtained.

If it is necessary to know the bulk volume of a brick to within 0.1 cc a correction must be applied for the buoyant effect of the air on the mercury and on the brass weights which are used in finding the weight of the moving system and in balancing the apparatus. This correction can be applied with sufficient accuracy in the case of standard straight bricks by subtracting 0.1 cc from the bulk volume as found above.

VI. Typical Bulk Volume Measurements

18. Typical Calculation A typical calculation of the bulk volume of a brick from the data secured from the mercury balance follows:

Wt. of brick..............	3,981.2 gm.
Balancing wt.............	3,831.5 gm.
Wt. of moving system......	14,000.0 gm.
	————————
Total thrust downward....	21,812.7 gm.
Temp. of mercury.........	27.5°C
Density of mercury (in vacuo)............	13.5276 gm.cc

Total vol. of mercury displaced* =
21,812.7 ÷ 13.5276 = 1612.5cc
Uncorrected bulk vol. of brick =
1612.5 − 0.75 = 1611.8cc
Buoyancy correction = 0.1 cc
Corrected bulk volume of
brick = 1611.7 cc

* If Landolt-Bornstein tables are available the total volume of the mercury displaced can be found by multiplying the "total thrust downward" (21,812.7 gm.) by the appropriate factor from Table 25 p. 78 of the 5th edition (1923), or Table 20 p. 47 of the 4th edition (1912).

19. Comparison of Caliper and Mercury Balance Measurements The bulk volumes of samples of typical fire brick were measured by means of the mercury balance and were also calculated from caliper measurements. The results are reported in Table I.

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[1] See §§15, p. 314.

TABLE I

MERCURY BALANCE AND CALIPER MEASUREMENTS OF BULK VOLUME

Sample	Type	Position	Bulk volume in cc	
			By mercury balance	By calipers
A 1	Fire clay	Trade mark up	1538.65	1534.44
A 1 (dup.)	Fire clay	Trade mark up	1538.45	
A 1 (dup.)	Fire clay	Trade mark down	1538.65	
CF	Bonded SiC		1611.8	1629.04
CF (dup.)			1611.9	
CF (dup.)			1611.8	
FE	Clay (insulating)		1406.0	1427.31
FE (dup.)			1406.0	

The duplicate measurements made on the same sample but on different days by means of the mercury balance show that the measurements can be duplicated to within about 0.1 cc or to within 0.007%; thus changes in volume of less than 1% could be measured with accuracy. Caliper measurements are sometimes higher and sometimes lower than the mercury balance measurements depending on the shape of the sample.

20. Measurements to Show Accuracy of Molding The accuracy of molding of some dry press bricks was determined by making bulk volume measurements on different samples of the same brands of brick. These measurements are given in Table II. The uniformity of volume is clearly indicated by the results.

TABLE II

BULK VOLUME MEASUREMENTS TO SHOW ACCURACY OF MOLDING

Brand	Sample	Type	Bulk vol. in cu. cm.
C	A	Bonded SiC	1610.2
C	F	Bonded SiC	1611.8
A	F	Bonded Al_2O_3	1645.7
A	E	Bonded Al_2O_3	1643.8
R	F	Recryst. SiC	1707.4
R	E	Recryst. SiC	1705.5

VII. Advantages and Limitations of the Mercury Balance

21. Advantages By means of the mercury balance bulk volume measurements can be made on standard bricks with little loss in time and with great accuracy.

In comparison with most of the other methods, the mercury balance method saves time in that no preliminary soaking and no subsequent drying or firing of the brick is necessary.

The mercury balance method is more accurate than the methods in use at present as bulk volume measurements on most bricks can be made to within 0.007%. The most accurate measurements can be made with comparatively smooth faced bricks such as fire brick and specialized refractories. With these the balance is sensitive to 0.5 gm. and measurements can be made to within 0.005%. With bricks that have an appreciably rough surface, such as is found on some types of insulating brick, the volume of mercury which the brick displaces depends to a noticeable extent on the depth to which the brick is immersed; this decreases the sensitivity of the balance to some extent, but the volume of a brick can still be determined to within 1 cc. The definition of bulk volume given in the introduction cannot be applied to bricks of this type with great accuracy because so many large pores are open at the surface of the brick that the bulk volume depends on where we place the outer boundaries of these pores. In a case like this, it seems to be a logical procedure to define the bulk volume of a brick as the volume measured by a mercury balance when the brick is immersed to a depth of $\frac{3}{4}$ inch in mercury. With bricks of this kind quicker readings can be made if the cross-sectional area of the bolts (4, Fig. 2) is increased, as then the decrease in the volume of mercury displaced by the brick as it sinks will be approximately balanced by the increase in the volume displaced by the bolts.

With bricks that are very permeable there will be some tendency of the mercury to penetrate the brick. A little penetration into a pore or crack of relatively small diameter introduces no error as the weight of any mercury that penetrates will be included in the weight of the brick and thus no error will be introduced.

The presence of impurities in the mercury will affect its density. This, however, introduces no serious difficulty as most fire brick contain no ingredients that are soluble in mercury and the cast iron trough is practically insoluble and if, consequently, the bricks are brushed well before being measured the mercury will remain sufficiently pure for a long time.

For $\frac{1}{100}$% accuracy it is only necessary to determine the temperature of the mercury to 0.5°C, for $\frac{1}{200}$% to 0.25°C. This can be done with sufficient precision as the mercury is well-stirred during the balancing process and has a high heat capacity.

22. Limitations The mercury balance is not recommended for measuring bricks that are badly cracked or have very large open pores as in such cases it is difficult to secure a good reading and difficult to recover the mercury which soaks into the brick. There may also be some very weak insulating brick which could not be measured in the mercury balance as they would break under the strain imposed.

Where only a few measurements are to be made the cost of the mercury and the necessity of building a special apparatus will prohibit the use of this method. However, as the apparatus can be built from readily available materials and the loss of mercury can be made very small, it can be used to advantage when many measurements are to be made.

USE OF EUTECTICS AS GLAZES[1]

By Hobart M. Kraner

ABSTRACT

The properties of the high silica eutectics of some of the common ternary systems are given consideration in suggesting them for use as glazes on ceramic bodies.

It is generally considered good practice to compound glazes so as to use several RO constituents rather than only one. The reason for this is that the viscosity is lowered thereby, and the greater the number of fluxes present, the lower the temperature at which fusion begins and the wider will be the range of temperature over which the solution of the excess constituents takes place. It has not been mentioned however that such practice also involves the use of a greater amount of excess, or relatively insoluble constituents such as alumina and silica. The net effect is therefore no different than may be found in a glaze which consists of a larger amount of a eutectic which melts at a higher temperature than the low melting constituent of the more complex glaze. A glaze containing only a small amount of a low temperature eutectic hardened by the presence of the large excess of material which passes into solution over a wide range of temperature may not reach maturity as a glaze any earlier than one containing a larger amount of a high temperature eutectic. For example, consider a glaze containing 10% of a eutectic melting at 900°C, and the glaze itself maturing at 1300°C. This means that the glaze has a range of 400°. Then consider a glaze containing 95% of a eutectic which melts at 1000°C and the solution of the whole composition being complete and mature as a glaze at 1100°C. In the latter case melting began later than in the former case but was completed earlier.

Eutectics are compositions having the lowest melting temperatures of their respective systems. Their vapor pressures are also the minimum and in such compositions therefore volatilization of the constituents is minimized. This is not as vital a consideration in glazes for porcelain as it is in the case of enamel compositions and very low temperature glazes where many volatile constituents come into use.

NOTE: In speaking of the properties of eutectics in this connection it must be remembered that the high viscosity, slow diffusion and low thermal conductivity of silicate melts (particularly those high in silica) precludes any attempt to claim that a eutectic mixture composed of ceramic materials poorly ground or mixed may act as a molecularly dispersed homogeneous mixture of the same fired composition. However, it has been repeatedly shown that a eutectic mixture composed of ceramic materials does have a much more rapid deformation than other compositions similarly prepared which are not eutectics. The viscosity and viscosity-temperature relations also affect certain interpretations in this connection. With all of these in mind it is hoped that the material presented will not be misleading or appear too presumptuous.

[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division). Received December 8, 1925.

In eutectic compositions the components are mutually soluble. If the temperature slightly exceeds the eutectic melting temperature, each of the constituents will pass into solution simultaneously; or in the case of a ceramic mixture, within only a few degrees range.

It has been pointed out by Vogt[1] that on cooling "compositions near the eutectic further the formation of glass." This should recommend them to a certain extent for use as glazes.

The foregoing seem to indicate a few favorable properties through which such compositions may find application. Riddle and Laird[2] have pointed out the contribution of glazes to the strength of porcelain. In cooling a glazed porcelain body from its maturing temperature, it first passes through a plastic or semi-plastic stage. Some place in this cooling the liquid becomes solid and the piece then shrinks according to the thermal expansion of the solid mass. In most cases the glaze is soft long after the porcelain mass has reached the rigid condition. Unless the glaze in the solid state has a very low coefficient of thermal expansion, it is under tension, and very probably adds strength to the porcelain tested in tension. In case the glaze does have a lower coefficient of thermal expansion than the body, the cooling below its solidification temperature will place it under compression and the body under tension. It would seem therefore that through the control of solidification temperature of the glaze, glaze fit and strength of porcelain may to a certain extent be affected independently of some of the other factors usually considered.

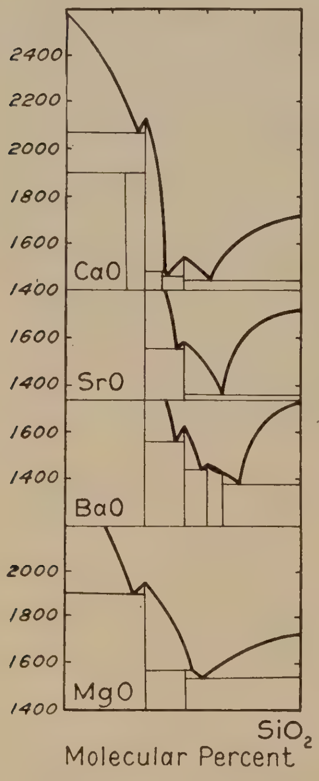

FIG. 1.—Eskola, *Amer. Jour. Sci.*, **44** (1922). Bowen and Anderson, *Am. J. Sci.*, **37**, 478 (1914).

In the case of chemical porcelain or spark plugs it would seem that a glaze having a high temperature of initial melting is more desirable than the usual type of glaze which is apt to be soft at the temperature at which it is to be used. The possibility of utilizing such a glaze of eutectic composition in this connection is very favorable due to its possible high temperature of melting with rapid rate of maturing.

Where a glaze free of or low in bubble content is desired, one having a late melting point may provide sufficient time for the decomposition of the glaze materials such as carbonates, nitrates, etc., which might ordinarily decompose at temperatures where the long range glaze has already become somewhat fluid. The result is that in the eutectic composition the probable large volume of gas has been easily liberated from the unfused glaze coating, and thereby does not interfere when melting begins. The body may also contain a large amount of bituminous material whose oxidation is not prevented as when an early melting glaze is used.

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[1] J. H. L. Vogt, *Jour. of Geol.*, **31** [3], 233–52 (1923).

[2] F. H. Riddle and J. S. Laird, *Jour. Amer. Ceram. Soc.*, **5**, 500 (1922).

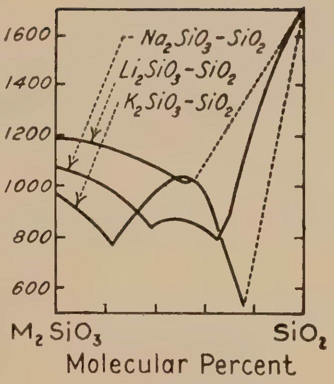

FIG. 2.—Morey and Bowen, *Jour. Phys. Chem.*, **28**, 11(1924).

Singer[1] states that for steatite or other high magnesia compositions the following or similar glazes high in magnesia should be used.

$$\left.\begin{array}{l} 0.876 \text{ to } 0.962\ MgO \\ 0 \quad\ \text{ to } 0.023\ CaO \\ 0 \quad\ \text{ to } 0.017\ Na_2O \\ 0.007 \text{ to } 0.046\ K_2O \\ 0.026 \text{ to } 0.030\ FeO \end{array}\right\} 0.058 \text{ to } 0.281\ Al_2O_3\ 1.476 \text{ to } 2.202\ SiO_2$$

The MgO-Al_2O_3-SiO_2 eutectic[2] melting at 1345°C and having the composition

$$\left.\begin{array}{ll} MgO & 20.3 \\ Al_2O_3 & 18.3 \\ SiO_2 & 61.4 \end{array}\right\} \text{has the molecular formula}$$

$$MgO \quad 0.38\ Al_2O_3 \quad 2.01\ SiO_2$$

This also is a good glaze at cone 14 but does not closely conform to the empirical rules given for the design of lime-feldspar porcelain glazes for that temperature. The feature of using a high MgO glaze is simply an application of the law of mass action. It is unlikely that there would be much interaction between glaze and body where their compositions are similar, and the possibility of obtaining a bright glaze on a similar body is favorable.

The use of a glaze in which CaO is the only flux is mentioned by Kerl[3] and this seems to be simply the high silica eutectic of the lime-alumina-silica system[4] hardened by clay and flint. Its formula is as follows:

$$CaO \quad 1.16\ Al_2O_3 \quad 8.98\ SiO_2$$

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[1] Die Keramic im Dienste von Industrie und Volkswirtschaft, p. 404.

[2] Rankin and Merwin, "The Ternary System MgO-Al_2O_3-SiO_2," *Am. Jour. Sci.*, **55** (1918).

[3] Handbuch der Thonwarenindustrie, p. 1401.

[4] Rankin and Wright, "The Ternary System CaO-Al_2O_3-SiO_2," *Am. Jour. Sci.*, **39** (1915).

The high silica eutectic in the lime-alumina-silica system melts at 1170°C. At cone 6 it is a good glaze. Its composition and molecular formula are as follows:

CaO	23.25
Al_2O_3	14.75
SiO_2	62.0

$$CaO\ 0.346\ Al_2O_3\ 2.48\ SiO_2.$$

Any addition or reduction of any of the three constituents of such a glaze will serve to harden it. The most satisfactory method of hardening most of these is through the addition of silica. A study of the lime-alumina-silica or the magnesia-alumina-silica systems will make this apparent. The lines connecting these respective high silica eutectics with silica represent compositions which are good glazes for many purposes.

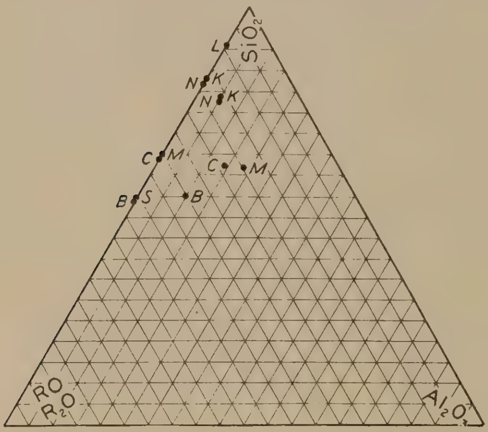

FIG. 3.

Attempts have been made to use old plaster of Paris molds as a glaze ingredient. Many of these attempts have met with failure due to the evolution of the SO_3 causing either bubbles, blisters, or scumming. The use of old molds in a glaze of the eutectic type using CaO as the only flux yields favorable results in spite of the information[1] which gives the

	BaO	SrO	CaO	MgO	Na_2O	K_2O	Al_2O_3	SiO_2	Deforms or Melts	Worker
B	47	....	....	....	....	....	....	53	1374	Eskola
B	35	....	....	....	....	....	10	55	Cone 6	Watts
S	..	46.5	....	....	....	....	....	53.5	1358	Eskola
N	..	....	....	....	18.4	....	....	81.6	860	Rice
N	..	....	....	....	17.5	....	5.4	77.1	800	Rice
N	..	....	....	....	17.64	....	....	82.36	802	Morey & Bowen
K	..	....	....	....	....	17.5	....	82.5	880	Rice
K	..	....	....	....	....	17.4	5.2	77.4	870	Rice
C	..	....	37	....	....	....	....	63	1436	Rankin & Wright
C	..	....	23.25	....	....	....	14.75	62	1170	Rankin & Wright
M	..	....	....	35	....	....	....	65	1543	Rankin & Merwin
M	..	....	....	20.3	....	....	18.3	61.4	1345	Rankin & Merwin
M	..	....	....	20.0	....	....	20.0	60.0	Cone 12	Watts

Eskola, *Am. J. Sci.*, 44 (1922).
Rice, *Jour. Amer. Ceram. Soc.*, 6, p. 480 (1923).
Watts, *Trans. Amer. Ceram. Soc.*, 19 p. 453–459 (1917).
Rankin & Wright, *Am. J. Sci.*, 39 (1915).
Rankin & Merwin, *Am. J. Sci.*, 45 (1918).
Morey & Bowen, *J. Phys. Chem.*, 28, 11, (1924).

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[1] Ingberg, *Trans. A. S. T. M.*, **23**, 254 (1923). Treadwell and Hall, Analytical Chemistry, Vol. 2.

decomposition temperature of $CaSO_4$ as being higher than the temperature of melting of the lime-alumina-silica ternary eutectic, at 1170°. It would be ideal in this case if the temperature of decomposition were below this temperature. However, since the melting is somewhat rapid, the SO_3 is liberated with the melting and a good glaze results within a few degrees of 1170°C.

When composed of old molds, clay, and flint this glaze is as follows:

Old molds ($CaSO_4\ 2H_2O$)	46.6
Clay	24.2
Flint	29.2

This glaze has been found satisfactory in regard to quality and to be practical in application as well as to reduce the glaze cost on ware such as standard dry press porcelain, etc.

Unfortunately the systems of all of the oxides of the alkaline earths and the alkalis with alumina and silica are not complete. A comparison of the binary systems as shown in Figs. 1 and 2 will show the similarity of positions of the high silica eutectics. Figure 3 shows another similarity of eutectic compositions which may prove of some benefit in the development of glazes of this type for special purposes. This indicates that even though these systems are not complete their ternary eutectics if desired are apparently easily available.

Westinghouse Electric and Mfg. Co.
East Pittsburgh, Pa.

A LABORATORY MUFFLE KILN[1]

By L. M. Merritt

ABSTRACT

The general construction of a gas-fired muffle kiln is discussed and its chief advantage is given in that it has a single piece, easily replaceable muffle with high heat conductivity.

Introduction

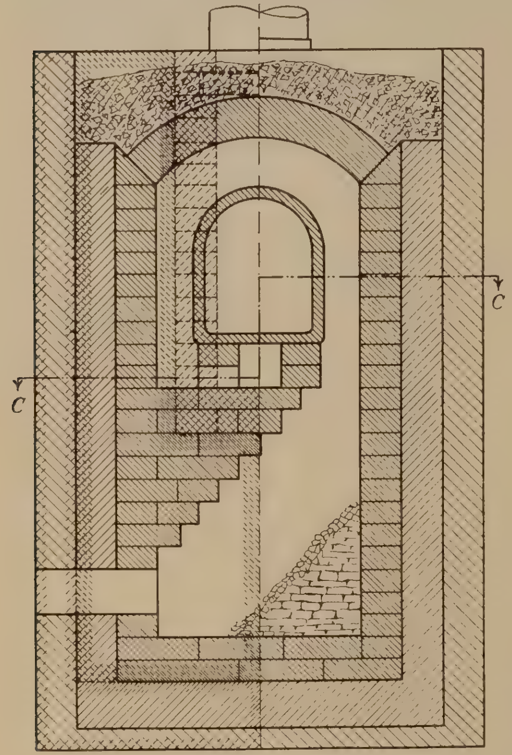
Many types of laboratory kilns have been designed for various uses. The object in mind when designing this kiln was to have one that would be practical in an ordinary plant. In order that this might be attained the following considerations seemed most important.

1. A kiln which would heat the same throughout the muffle.
2. A kiln which would heat up quickly with a low fuel cost.
3. A muffle in one piece.
4. A muffle which could be made in any sagger room by the plant sagger makers.
5. A muffle which could be changed easily without loss of time.

It has been attempted to incorporate these into the design.

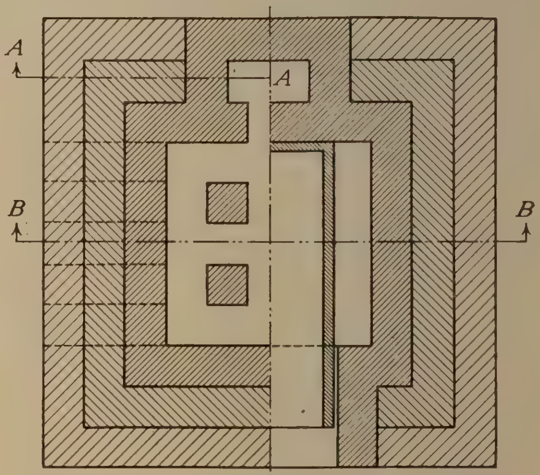
Construction

The accompanying sketches show the construction of the kiln. For cone 4 temperatures, a wall consisting of $4\frac{1}{2}$ inches fire brick, $4\frac{1}{2}$ inches insulation and 4 inches common brick has proved very satisfactory.



Section at B-B shown by solid lines
" " A-A " dotted "

FIG. 1.



Section C-C

FIG. 2.

Section *BB* shows a vertical cross-section of the kiln; Section *A* the outlet gas flue and the regulating damper; Section *CC* the muffle support and the horizontal flue leading into the stack.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. Received January 8, 1926.

Gas is burned in either two or three burners dependent upon the temperature to be attained. For cones 2 to 4 two burners will bring the temperature in 24 hours. Above cone 4 three burners are required. A bed of alundum chips made from broken grinding wheels assists the burners in getting complete combustion in the base of the kiln. A stack 15 feet high and 10 inches in diameter furnishes sufficient draft.

The combustion gas flow is around the entire muffle going up one side and down the other to a cross flue under the muffle. This cross flue leads into the stack and the draft is regulated by a damper, made from an 18 x 12 x 2½-inch fire slab.

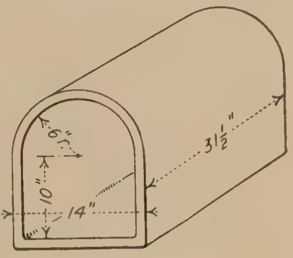

FIG. 3.

The muffle is made in one piece with one end closed as shown by the muffle detail. This piece was made over a form similar to a handmade sagger form. The routine of the sagger maker was followed exactly, first batting out the base, side, and ends and then welding the parts together in the same manner as the sides and bottom of the sagger are stuck together. This was fired in a kiln in the same manner as green saggers. The muffle rests on a base which is corbelled out from the side and tied into both ends. The muffle extends into the doorway nine inches and stiff fire clay is packed between the brick wicket and the muffle. In mudding up the door I always build a double door, one in the muffle and the other outside in the wicket. Thus a double seal of furnace gases is obtained.

The entire kiln is securely tied together by three sets of tie rods drawn tightly at the corners which are reinforced with 3x3x⅜-inch angles.

Advantages and Uses

The muffle can be renewed easily when a crack appears by just breaking up the old muffle and taking it out in pieces. Then a new muffle can be slipped into place and a little mud packed in on the side to make it gas tight. This eliminates one of the big disadvantages of most of the other types of muffle kilns of the same size and capacity.

Another advantage is the even heating of the muffle. Since the walls of the muffle are thin (about 1 inch) conductivity is high and the temperature variation between the outside and the inside of the muffle is at a minimum. A carborundum muffle would have longer life and higher conductivity than a fireclay or sagger batch muffle. The combustion gases have a long travel, wrapping almost entirely around the muffle.

It appears that many plants manufacturing clay products could use a small muffle kiln of this type to advantage for testing and checking batches and new raw materials. This is especially true in the terra cotta industry where nearly all of the products are fired in muffles.

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COLUMBUS, OHIO

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ORIGINAL PAPERS

INTERFEROMETER MEASUREMENTS OF THE THERMAL DILATATION OF GLAZED WARE[1]

By G. E. Merritt and C. G. Peters

ABSTRACT

The network of fine cracks often seen in the surface of glazed products not only mars the surface but shortens the life and lowers the price of the ware. Since the relative expansivity of the glaze and body is a very important factor in controlling this condition reliable measurements of both are of the utmost importance. Until recently the difficulty has been that the expansivity of the glaze has been measured on specimens of the material melted to glass and drawn into rods or cast in molds of sufficient length. Owing to the difference between this treatment and that received by the material when spread on the ware, it was realized that these methods might lead to unavoidable errors.

By the interference method, specimens 0.2 mm. in length can be measured with sufficient accuracy. Therefore in measuring glazes the samples may be taken directly from the finished ware. In this paper the thermal expansion of glaze materials prepared in the form of drawn glass or cast rods is compared with that of the same material taken from the finished ware. From the measurements, the expected divergence is found to be as much as 20% in the case of drawn glass specimens, and 10% for cast specimens.

I. Introduction

Glazed ware, which consists of a body such as terra cotta, white ware, porcelain, etc., covered with a thin layer of glazing material, very often cracks or crazes when subjected to temperature changes or even when allowed to stand for a period of time. The large percentage of such failures in glazed ware has been, and is still, a serious matter and is responsible for enormous losses to builders and other users as well as to the ceramic industry.

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Terra Cotta Division). Received April 26, 1926.

Cause of Crazing The crazing of a glaze doubtless results from the stresses set up by unequal expansion or contraction of the glaze and body. The capacity of a glaze to withstand these stresses depends upon its tensile strength, elasticity, thickness, and its adherence to the body. Being very brittle and in a layer only a few tenths of a millimeter thick, it cannot be expected to withstand large distorting forces. It follows that the most effective way to decrease the number of failures is to reduce the stresses below the yield point of the glaze. Stresses may arise from unequal expansion (or contraction) of the glaze and body caused by temperature change, by body absorption of moisture, by crystallization, or by compressive forces on the body. Dimensional changes of the body arising from crystallization which are sufficient to produce crazing are probably of rare occurrence. Material absorption of moisture by the body can only take place after the glaze has already cracked. The unequal thermal contraction of the glaze and body during the final cooling from the softening point of the glaze to room temperature is, in many cases, sufficient to produce forces capable of cracking or crushing the glaze. Hence, before more complicated causes of the failure are sought for, a close match in the thermal contractions of the glaze and body under the final cooling treatment over this entire temperature range must be attained, by the use of the right materials and treatment. This requires accurate data on the thermal expansions of both the glaze and body of the finished ware.

Measurement of Expansion Expansion measurements in previous investigations have been made with some form of micrometric apparatus which requires specimens 4 inches or more in length and at least $\frac{1}{4}$ inch in diameter. Since it is impossible to take samples of that size from the glaze of the finished ware the glaze batch material has been either melted to a glassy consistency in crucibles and drawn into long rods or cast in molds. It seems reasonable to suspect that the expansions of specimens made by either of these methods would not be the same as the expansion of the glaze on finished ware.

In firing, considerable interchange of constituents doubtless occurs between the thin layer of glaze and the body material, which makes the composition of the final glaze different from that of the cast or drawn specimens. Also the final heat treatment of the ware may be very different from that of the cast or drawn specimens thereby producing dissimilarities between their physical properties and those of the actual glaze. Tool and Eichlin[1] have shown that wide variations in some of the physical properties of glass can be produced by different heat treatments even when no change in the composition of the material has taken place.

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[1] Tool and Eichlin, *Jour. Op. Soc. Amer. and Rev. Sci. Inst.*, **8**, 419 (1924).

With the interferometric method described in Bureau of Standards, Scientific Papers, Nos. 393 and 485, the thermal expansion of specimens ranging in length from 0.2 to 10.0 mm. can be measured with sufficient accuracy in the temperature interval, 20 to 1000°C. Using this method in the present investigation, measurements were made on the expansivities of samples of the body and glaze taken from the finished ware and of cast and drawn specimens made from the same batch mixture as the glaze. This makes it possible to compare the expansivities of samples, made in the three different ways from the same glaze material, with each other and with the expansion of the body. These comparisons show that the expansion of the cast or drawn specimens may be very different from that of the glaze and that the specimens must be taken from the finished ware if reliable data is to be obtained. They also show that unless the expansivities of the glaze and body when subjected to the particular heat treatment used in making the ware, are nearly the same, stresses sufficient to produce crazing will arise.

Preparation of Samples

Six different batch mixtures of glaze material, the compositions of which are given in Table I, were prepared and specimens of each were made by the three following methods. These specimens will be referred to as: (1) drawn glass, (2) cast, and (3) glaze, specimens.

(1) Drawn Glass Specimen The glaze batch material was fed into a porcelain crucible heated in a gas-fired furnace until a clear melt was obtained. An iron bar or pincers was then thrust into the pot and a rod of the glass drawn out. Three sections, each about five millimeters long, cut from this rod, constituted the specimen.

(2) Cast Specimen Glaze material was piled on a V-shaped groove in the upper face of a porcelain block and fired in a kiln to the temperature at which the glaze was supposed to mature. Three fragments broken from this cast were used for the specimen.

(3) Glaze Specimen Plates of ordinary table whiteware or blocks of terra cotta were first glazed with the material. The type of bodies chosen and the technique employed duplicated common commercial practice. A sample of the glaze 0.2 to 0.4 mm. thick was broken from the surface of the finished ware and freed from any adhering fragments of body. A microscopic examination insured removal of the undissolved body. Three fragments of the resulting flake of glaze were used for a specimen.

Table I

	A	*B*	*C*	*D*	*E*	*F*
SiO_2	54.6	52.0	49.7	47.4	60.5	52.0
Al_2O_3	8.7	8.5	12.7	9.2	14.9	9.1
CaO	8.6	7.9	7.0	9.6	10.4	7.0
PbO	16.3	15.6		15.6	11.3	16.0
ZnO	3.6	4.1	3.4	5.4	2.9	3.2
SnO_2	0.2	0.1		0.2		0.2
K_2O	0.7	2.4	9.7	0.3		0.1
Na_2O	0.7	2.4		3.6		3.4
B_2O_3	6.6	7.0		8.7		9.0
MgO			1.7			
BaO			15.8			

Experimental Method of Procedure

In each case the prepared specimen was placed between two fused quartz interferometer plates and heated in an electric furnace at the rate of 2.5° per minute to some temperature above the annealing range of the glaze. The heating current was then cut off and the sample allowed to cool in the furnace. The rate of cooling at the start was about 5° per minute. During both heating and cooling, the temperatures and the changes ΔL in the length, L, of the sample were recorded as the interference fringes passed a reference mark on the upper plate.[1] The first run was followed by a second taken over the same temperature range and using the same heating and cooling schedule.

Since the strains that crack the glaze are set up during the final cooling of the finished ware, it is essential to have the expansivities of the glaze and body match during that process. We have found from repeated runs on various materials that the expansion of any particular heating is usually very similar to the contraction of the cooling immediately preceding and supplies more information regarding the effects of that cooling treatment than any subsequent heating or cooling data. From this it follows that the first heating curve furnishes valuable information about the way the samples contracted when cooled during the process of manufacture. The second runs give the expansivities of the samples after they had all received practically the same heat treatment as a result of the first runs. The differences in the first run expansivities may be caused by differences in the composition and the final heat treatment, resulting from dissimilarities of the three methods of producing specimens from a given glaze material. The

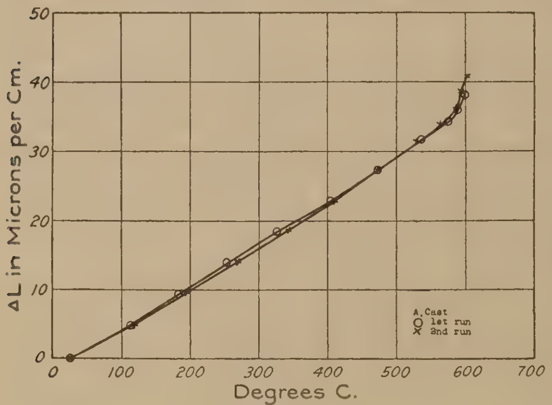

FIG. 1.

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[1] See Bur. Stand., *Sci. Paper*, No. 393 for a description of the apparatus.

second run, however, is taken after the specimens have all received nearly the same heat treatment as a result of the first runs, hence any differences in the expansions of the specimens prepared by the three methods must be ascribed to differences in composition or molecular arrangement.

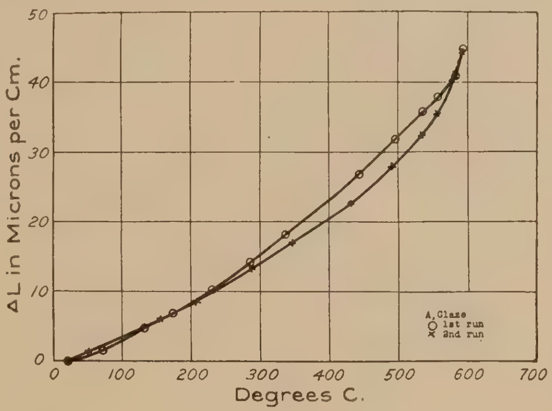

FIG. 2.

These changes in composition may be caused by the volatilization of certain constituents, by the absorption of impurities from the body or by contamination by furnace gases. The possible differences in the combinations between the constituents may be modified by such changes in composition or by the temperature and time required in the production of the sample.

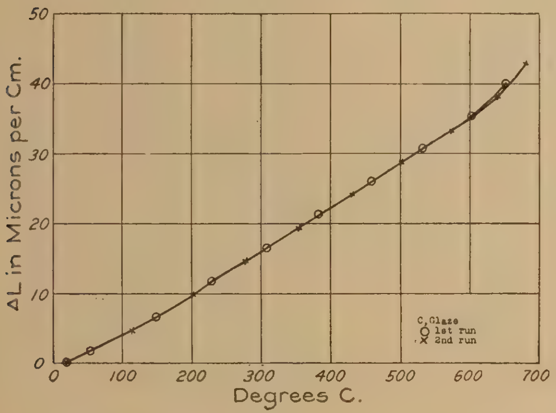

FIG. 3.

Experimental Results

Figures 1 to 7 inclusive show measurements obtained by first and second runs on several samples. In some cases the expansion during the second heating was nearly the same as during the first, while in other cases the expansivity was changed considerably by the treatment received during the first run. With glaze material *A*, the curves from the two runs on a cast sample, Fig. 1, are nearly the same while those for the glaze sample, Fig. 2, are different. In the case of glaze material *C*, the reverse is true. The results from the two runs on the *glaze* sample, Fig. 3, are almost identical while those for the *cast* specimen, Fig. 4, are very different. The curves representing the results from the first and second runs on the cast specimen, Fig. 5, from glaze material *D*, agree very well; while those for the drawn sample, Fig. 6, diverge at

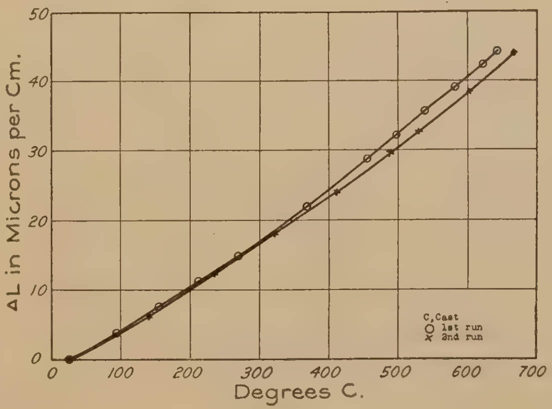

FIG. 4.

about 400°C. The rod from which the drawn sample was taken must have been cooled quickly when drawn from the pot, otherwise the drop in the expansivity above 500° similar to that shown by chilled glasses could not be accounted for. The curve representing the second run shows the effect of the annealing treatment received during the first run. Data obtained from the first run on samples of this kind would be of little value in matching expansivities of glazes and bodies.

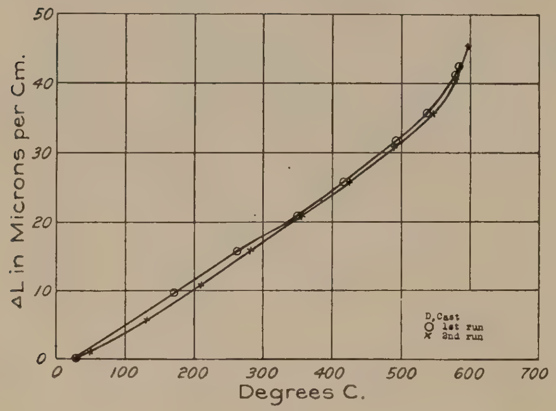

FIG. 5.

The two curves shown in Fig. 7 represent the results from the first and second runs on a sample taken from the body that was used with glaze *D*. The expansion of the first run shows a large decrease between 100 and 300°C and a rapid increase in the $\alpha-\beta$ quartz transformation region. In the second run, the expansion did not decrease in the lower region, but increased as before near 575°C. These two curves are typical of results we have obtained from first and second runs on a large number of body materials and suggest that the peculiar expansivity of the body may be responsible for some of the difficulty in matching glazes and bodies.

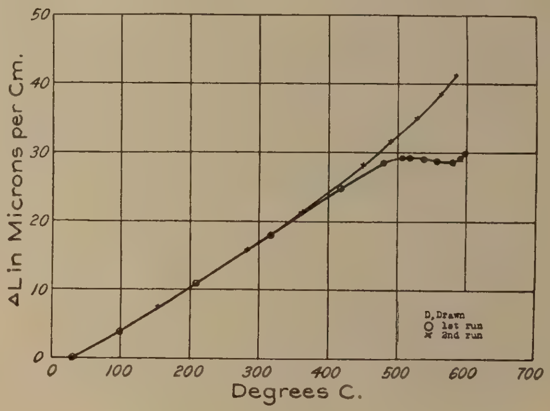

FIG. 6.

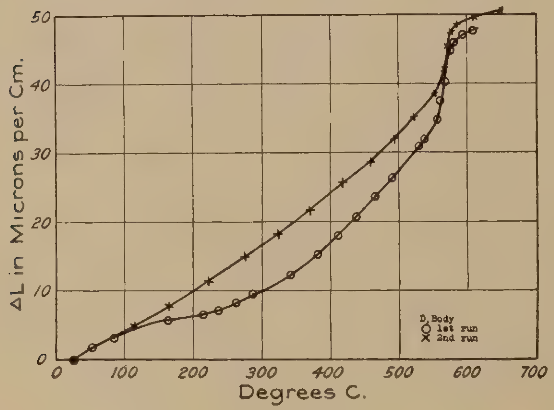

FIG. 7.

In the ten figures, 8 to 17 inclusive, are two for each glaze batch mixture, one of which represents the results from the first runs on specimens prepared by the three methods and the other, the second runs on the same specimens. If either a cast or a drawn specimen is to give the correct thermal expansion of the glaze, the result from the first run must agree with that of the first run on a glaze sample taken from the finished ware. In case there is a disagreement, the dissimilarity may be caused by differences in the previous heat treatment, the composition or the molecular arrangement, all of these differences being produced by the manufacturing process used.

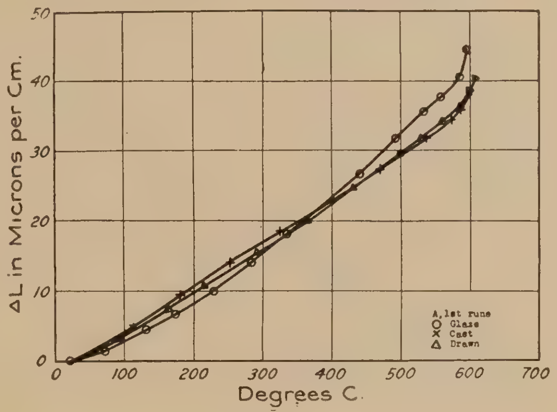

Fig. 8.

The same heating and cooling schedule was maintained during the first run for all the samples from a given batch. The rate of heating and cooling was low enough so that any effects of sudden cooling during the process of manufacture should be removed, thus leaving the samples in a fairly well annealed condition.

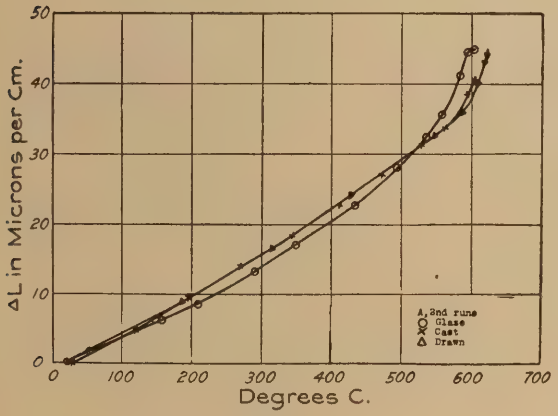

Fig. 9.

The figures representing the second runs are included to show the expansion of the samples made by the three different methods after they had all received the same annealing treatment. Since, as stated, the first run largely eliminates the differences arising from heat treatment, any difference in the second run expansions of the samples made by the three methods from a given batch mixture, indicates a difference in the composition or molecular arrangements of the three types of specimens. If such differences in composition are found, the inadvisability of using results from cast or drawn specimens to represent the expansivity of the glaze becomes evident.

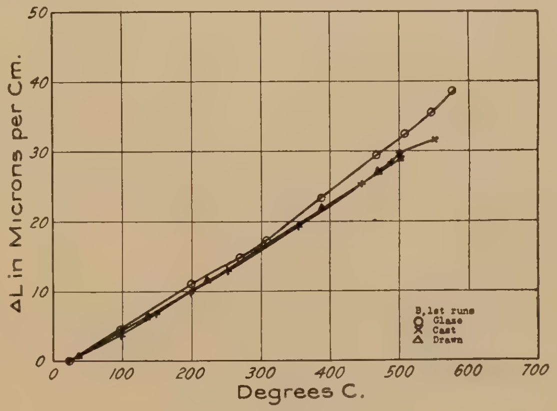

Fig. 10.

The first runs on the three types of specimens from batch mixture *A*, Fig. 8, show that the expansions of the cast and drawn specimens are nearly the same and that both differ considerably from the expansion of the glaze. The second runs on *A*, Fig. 9, show even a better agreement between the expansions of the cast and drawn samples. The shape of expansion curve and amount of expansion from 20 to 600°C are, however, very different for the glaze from what they are for either the cast or drawn specimens.

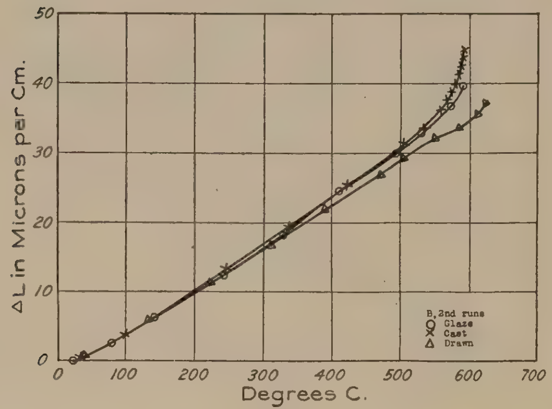

Fig. 11.

The expansions of the first runs on the cast and drawn specimens from batch mixture *B*, Fig. 10, are similar and both differ from the expansion of the glaze. The second run of the glaze and cast samples of *B*, Fig. 11, are nearly alike, but the cast one shows a lower annealing temperature. The drop between 550 and 600°C in the curve from the drawn specimen shows that the effects of chilling had not been entirely removed by heating to 500° during the first run.

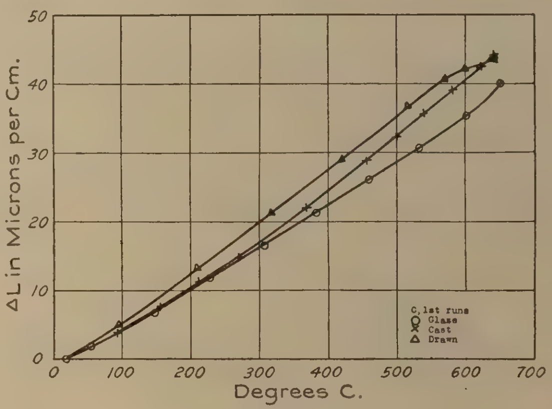

Fig. 12.

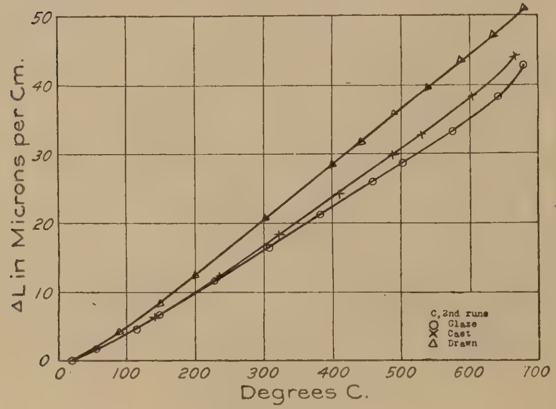

Fig. 13.

With batch mixture *C*, Figs. 12 and 13, the heat treatment given in preparation produced an effect tending to neutralize the effect of change of composition, so that the curves for the second run diverge from each other more than those of the first. Note that the cast and drawn specimens differ from each other as well as from the glaze both in the first and second runs. This may be ascribed to greater loss of volatile constituents and to other changes due to heat in the case of the drawn specimen, since it was necessarily heated to a higher temperature than the cast. A difference in the expansivities of a body and its glaze comparable with the differences exhibited by these specimens would doubtless cause crazing. For batch mixture *D*, Figs. 14 and 15, the expansion of the glaze and cast specimens show about the same divergency for both the first and second runs. This may indicate that their original heat treatments were similar, but that the composition of the glaze was very different from that of the cast specimen. The expansion of the drawn specimen decreased rapidly between 500 and 600°C during the first run showing the specimen was badly chilled. For determining the expansivity of a glaze, data from the first run on a chilled sample like this are worthless, since glazes are almost always annealed to a much greater degree. They are only valuable for showing the poorly annealed condition of the drawn specimen.

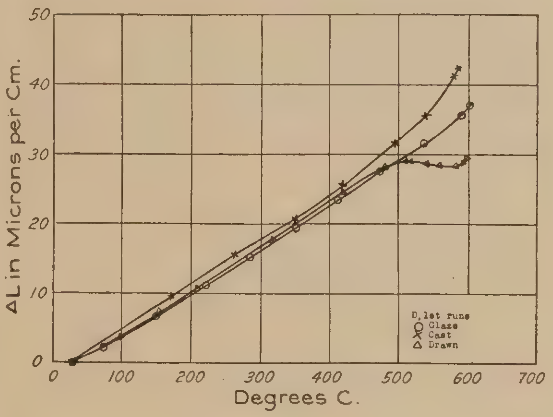

Fig. 14.

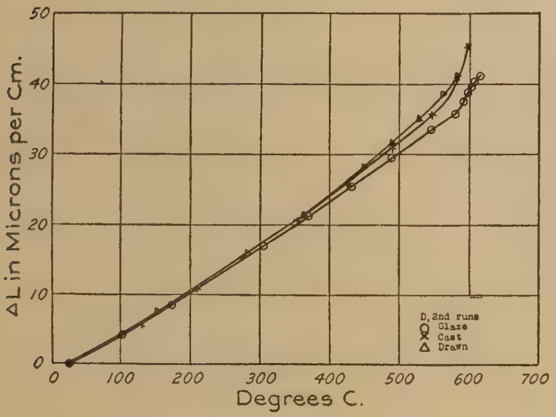

Fig. 15

The results from the first runs on the three samples of batch mixture *E*, Fig. 16, agree reasonably well. The poor agreement of the results from the second run, Fig. 17, show, however, that the similarity of the first runs were only a chance effect of heat treatment. A difference in composition or character of the glaze and cast and drawn specimen is evident.

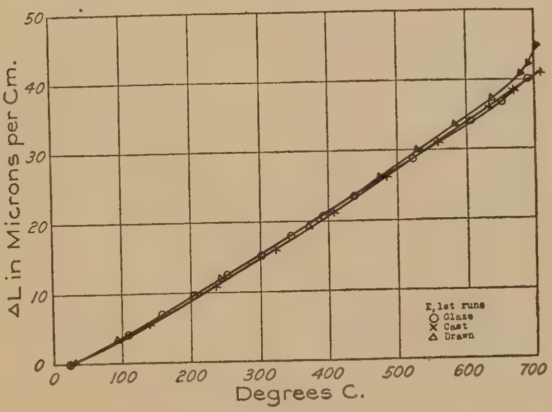

Fig. 16.

Discussion

The data presented thus far show that the thermal expansion of a given sample is affected by its previous heat treatment and that its final composition and molecular arrangement depend upon the method of production. From this it is evident that drawn specimens which, as a rule, are chilled, should not be used under any circumstance and that even the second run on the glaze sample should not be taken as representing the expansion of the glaze on the finished ware. The results from the second runs on each batch mixture show that the composition and molecular arrangement of glaze is different from either the cast or drawn specimen. This makes the use of either of the two latter types an unsafe procedure.

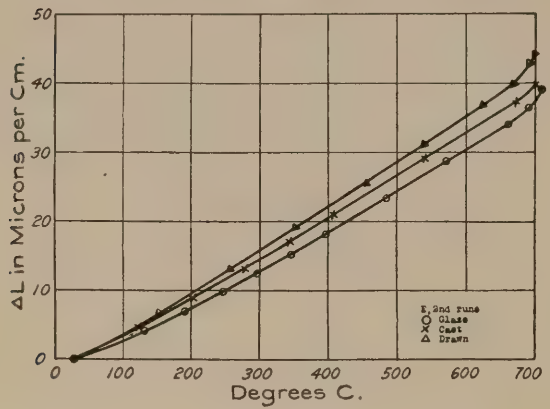

FIG. 17.

Check on Methods To show that the inconsistencies in the expansions in these different types of samples made from a given batch mixture were not caused by errors in the method of measurement or lack of homogeneity in the glaze, measurements were made on samples of glaze taken from different parts of the same brick. The crosses and circles, Fig. 18, represent the expansions during the first runs on two separate samples, both taken from the surface of a brick that had been glazed with batch mixture *C*. The second runs on the same two samples are shown in Fig. 19. The agreement between the two samples is very good in both cases. The first and second runs agree with each other showing that the brick had been cooled slowly. Measurements taken in the same way on two samples from a brick glazed with batch mixture *E*, are shown in Figs. 20 and 21. Here the agreement between the first runs on the two samples is excellent. The second runs are nearly the same. The first runs, however, differ somewhat from the second indicating that this brick must have cooled more rapidly than *C*.

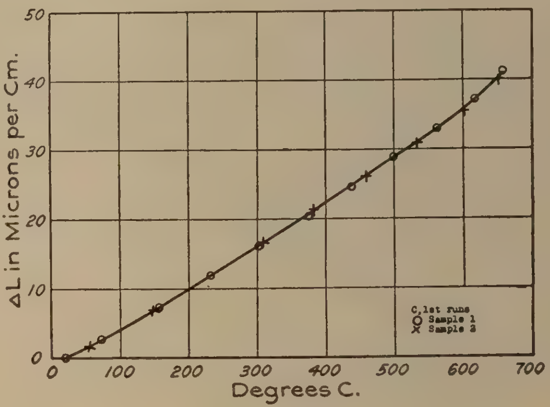

FIG. 18.

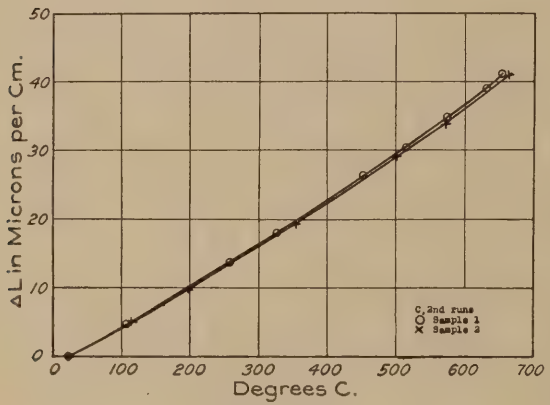

FIG. 19.

Expansion Normal vs. Parallel to Surface

Owing to the thinness of the glaze taken from the finished ware, the three pieces forming the specimens were broken from a flake and the expansivity was measured in the direction normal to the surface of the glaze. Since it is the expansivity parallel to the surface of the glaze that must match the expansion of the body, the objection might be raised that the measurements made normal to the surface do not represent the expansion of the glaze. Measurements were, therefore, made in both directions on samples from a brick glazed with batch mixture *E*. For the first run, Fig. 22, the expansion perpendicular to the glaze surface is represented by circles and that parallel to the surface by crosses. The second runs on the same two samples are shown in Fig. 23. From the close agreement of these results, it appears that no directional difference in the expansion of the glaze exists.

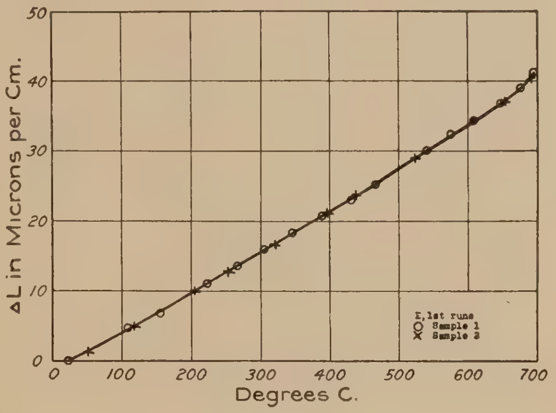

FIG. 20.

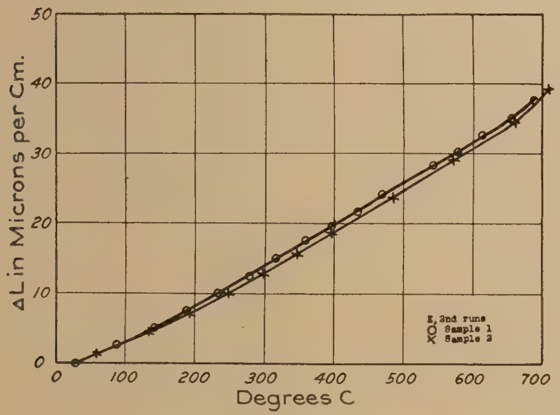

FIG. 21.

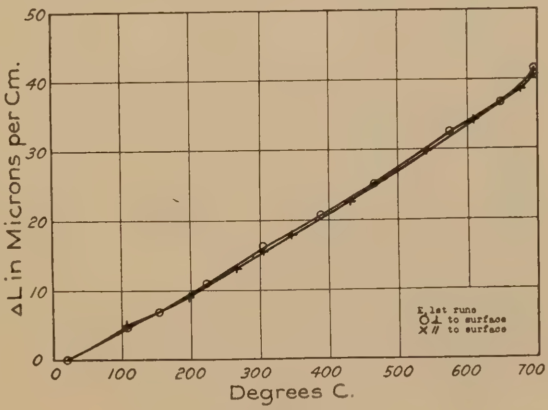

FIG. 22.

What appears to be a still more drastic test was made by using the samples from drawn rods. These were selected because of their rapid and unsymmetrical cooling which made it seem probable that these specimens, if any, would show a directional difference in expansion. Figure 24 gives the results of two first runs on samples from the same drawn rod, the crosses representing measurements parallel to the axis of the rod and the circles, those taken radially. Figure 25 shows results of the second runs on the same samples. It will be noticed that although results of the first and second runs are very different, the first runs on the two samples agree closely with each other and the second runs on the same samples show equally good agreement.

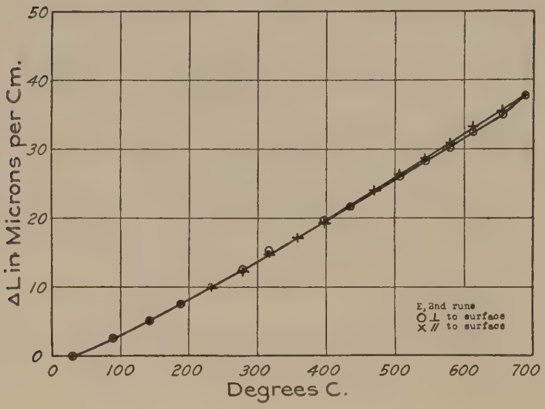

FIG. 23.

The Figs. 26 to 32 inclusive, show comparisons between the expansions of cast and glaze samples of batch mixtures, *A*, *D*, and *F* along with the expansions of bodies from which these glaze samples were taken. The results from first runs are used in each case because, as previously stated, they represent the best obtainable values of the contractions during the preceding cooling. The curves for the glaze and body are brought together in the annealing range of the glaze and from that point to room temperature they should represent closely the contraction of the glaze and body during the final cooling of the ware. The temperature where the curves should be made to coincide is of course, the one where, under a given cooling rate the glaze becomes more or less rigid, thus starting the accumulation of stresses. To determine this temperature and successfully interpret the expansion curves requires knowledge of several of the physical properties of the glaze, exact data on the cooling schedule of the ware and considerable experience in making thermal expansion measurements.

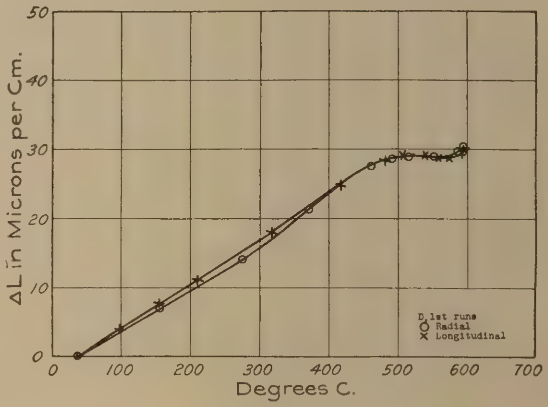

FIG. 24.

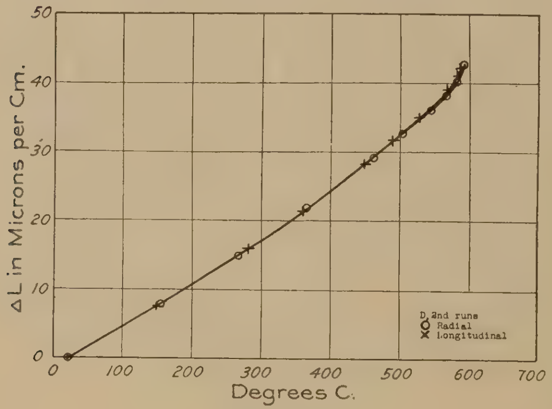

FIG. 25.

Temperature at Which Stresses Start to Accumulate

In a previous paper on the thermal dilatation of glass[1] the relation between the deformation from constant pressure and expansivity is given for several glasses at high temperatures. We have continued this work on glaze and other glasses during the past few years and our results show that all glasses exhibit comparable characteristics. From room temperature to the critical region, which is usually located somewhere in the range from 450 to 600°C depending on the composition of the material, the glasses expand at a nearly uniform rate and appear to be very rigid. Through a critical region of approximately 75° the glasses or glazes expand rapidly and soften at a rate that accelerates with the rise in temperature. Above the critical region the rate of expansion appears to become about the same as it was in the lower interval and the softening continues to increase rapidly. The annealing range is usually considered to include the lower half of the critical region and to extend somewhat below it.

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[1] Peters and Cragoe, Bur. Stand. *Sci. Paper*, No. 393, pp. 476–80.

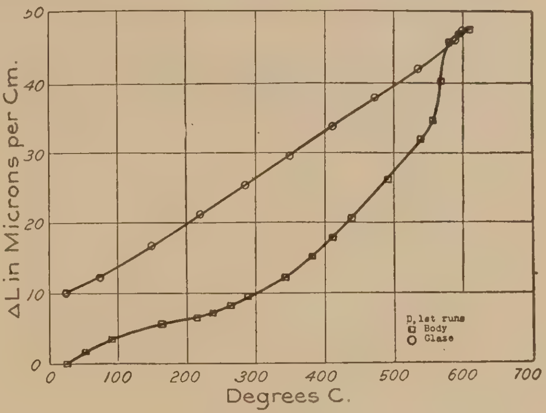

FIG. 26.

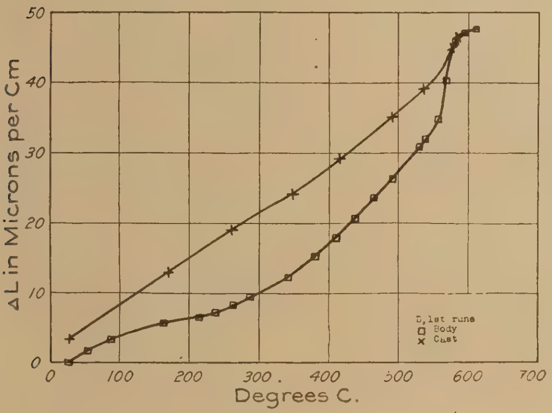

FIG. 27.

The glass samples and quartz plates fuse together at temperatures above the critical region. With the glass in the form of a solid ring, a large differential expansion exists between it and the plate because of the low expansivity of the quartz. On cooling through the critical region, it is found that on reaching the upper end of the annealing range, the glass becomes rigid enough to produce forces sufficient to bend the quartz plates as indicated by a change in the shape of the fringes. The plates continue to bend until the temperature falls to about the lowest limit of the annealing range

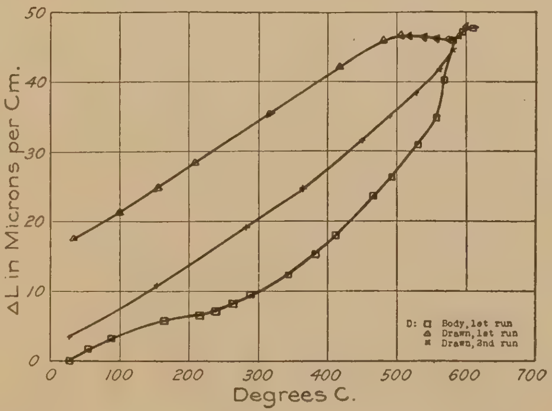

FIG. 28.

or to a point just below the bend in the expansion curve, when a rupture of either the plates or ring takes place.

From these observations it can be estimated with reasonable certainty that the temperature at which stresses start to accumulate in a glaze, in case it contracts differently than the body, is about 20° above the beginning of the critical region or near the upper limit of the annealing range; and furthermore that a differential contraction of about 5 microns to the cm. is sufficient to produce cracks in the glaze.

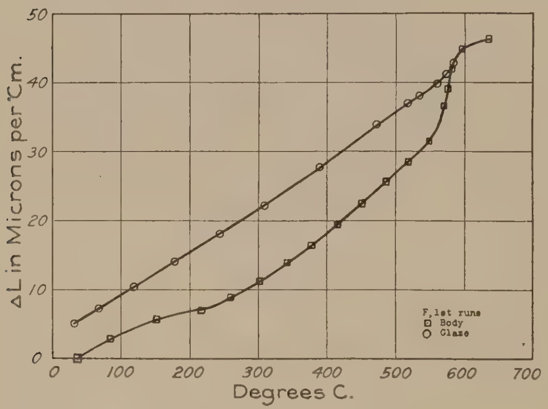

FIG. 29.

Effect of Difference in Expansion of Body and Glaze

The first run expansion of samples of body and glaze, *D*, taken from a plate that had crazed badly is shown in Fig. 26. The curves are brought together in the annealing range of the glaze and should represent closely the contractions of the glaze and body during the final cooling of the ware. These data show dimensional differences between the glaze and body of 17 microns per cm. at 350°C and 10 microns per cm. at 20°, which is ample explanation for the crazed condition of the plate. Figure 27 shows a comparison between the same body and the cast sample from batch mixture *D*. The expansion of the cast specimen agrees with the body expansion much better than does that of the glaze, especially at room temperature. An attempt to compare the expansions of the body and drawn specimen of batch *D* is made in Fig. 28. The results from the first run show the chilled condition of the drawn sample and demonstrate the unreliability of conclusions drawn from data obtained from that kind of specimen. Even the results from the second run do not agree with those from the glaze.

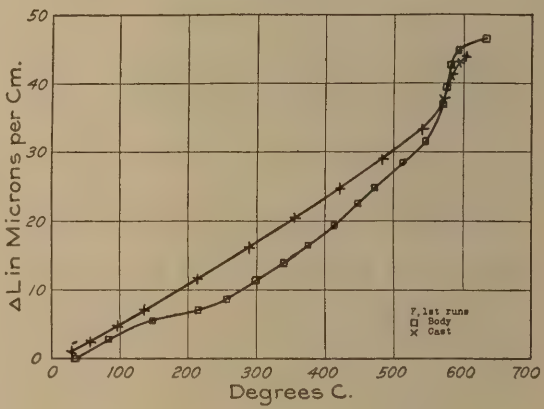

FIG. 30.

Figure 29 shows a comparison between the expansion of the body and glaze specimens of batch *F*, taken from another plate that crazed. The separation of the expansion curves shows that crazing should occur.

The agreement between the same body and the cast specimen of batch *F*, Fig. 30, is close enough so that a product free from crazing should be expected.

The expansions of the body and a glaze sample of batch *A* taken from a plate that did *not* craze are shown in Fig. 31. From the close agreement of the expansion curves a product free from crazing should be expected. It is doubtful if a closer match between any glaze and a body of this type could be obtained. On the other hand the results from the cast sample of batch A, Fig. 32, and the same body do not agree. The separation of curves would lead to the conclusion that the glaze should be crazed.

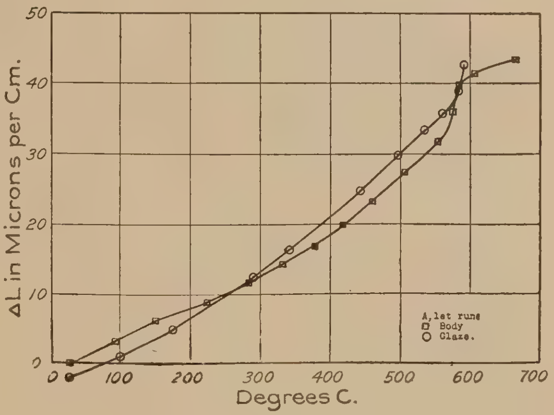

FIG. 31.

These comparisons of the expansions of glazes and bodies show that in the cases where crazing occurs there is a large difference between the expansions of the glaze sample and the body, while in the uncrazed ware a good match is found between the expansions of the glaze and body. In the cases of both the crazed and uncrazed ware, the cast specimens indicated conditions opposite to those actually found.

It will be noticed that the nature of the crazing, *i.e.*, whether tensional or compressional, should be indicated from the same curves. These, in Figs. 26 and 29, show that the body material contracted more than the glaze in the case of the two crazed plates. The glaze should therefore be under compression and develop compressional cracks. On examination this proved to be the case. Viewing the image of a straight edge at almost grazing angle from the surface of the plate, it was found that the glaze was thrust up on one side of the cracks and down on the other, which is a distinguishing characteristic of cracks caused by compression. Furthermore, examination with a microscope showed that the cracks were tightly closed and in no case showed an opening such as would have existed had the glaze pulled apart.

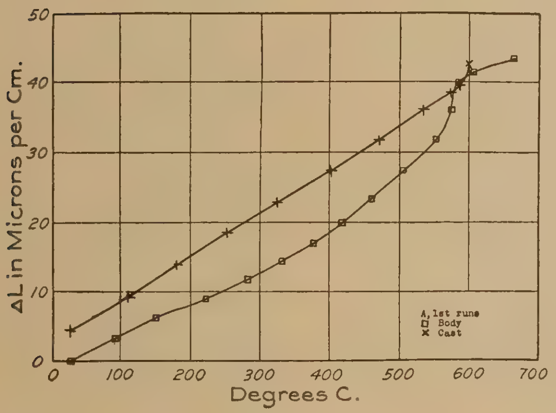

FIG. 32.

Measurements made on cast or drawn specimens cannot be relied upon to give the expansivity of the glaze on the finished ware.

To prevent crazing the expansion of the glaze from the finished ware must match that of the body.

Summary

To show the effect on the thermal expansions of different methods of preparing specimens of glaze, measurements were made by the interference method on the thermal expansions of six separate glazes representing two very different types, each prepared by three methods. Drawn glass specimens were made by melting the glaze material and drawing it into rods; cast specimens were melted into grooves in porcelain blocks, while glaze samples were taken from the finished ware.

Samples of the body were taken in several cases and their thermal expansions measured by the same method. The curves show that the condition of the finished product may be explained from the measurements on the glaze taken from the body, while the results of the measurements on specimens of cast or drawn material of the same batch composition were decidedly misleading.

The comparisons prove that the specimens must be taken from the ware if reliable data are to be obtained. They also show that the expansions of the glaze and body must be nearly the same if stresses sufficient to produce crazing are to be avoided.

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THE ELECTRICAL RESISTIVITY OF SOME CERAMIC MATERIALS AT ELEVATED TEMPERATURES AND A SIMPLE COMMERCIAL METHOD FOR ITS DETERMINATION.[1]

By Robert Maynard King[2]

ABSTRACT

This paper gives the values obtained by some resistivity measurements of several well known minerals used in the ceramic field. The values for some ceramic bodies are also given. A simple apparatus and method with which these values were obtained are described in detail.

Introduction

Many methods have been developed and used for the determination of the electrical resistance of ceramic materials and bodies at elevated temperatures. All of these methods are based on the assumption that Ohm's law holds for mineral compositions as well as for metals. This assumption is only approximately correct because of the physical and chemical changes which take place in heterogeneous mixtures. These changes are due to the passage of the current itself and to the effect of heat.

The methods developed by the Bureau of Standards,[3] by Brace,[4] and by Northrup[5] have been reviewed by Henry.[6]

These methods differ in detail, but in each case the outstanding problems are: (1) the assembly of an electrical measuring circuit which is sufficiently sensitive to measure accurately the small currents obtained and (2) the procuring of good contact between the terminals of the measuring circuit and the test piece. Since the method here described was developed to obtain reasonable accuracy only, strict scientific precision was not attempted. However, all precautions were taken which were consistent with simplicity and the desired accuracy.

It was found that a high resistance voltmeter was sensitive enough to obtain sufficiently accurate readings. A molten metal terminal such as was used by the Bureau of Standards[7] is the most satisfactory but its use was prohibited in this case because it was necessary to use porous test pieces. Henry[1] used a layer of lamp black between the graphite terminals and the test pieces, but this created a reducing atmosphere and was not employed since oxidizing conditions were desired.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (White Wares Division.) By permission Director, U. S. Bur. of Mines.

[2] Coöperation research engineer, U. S. Bur. of Mines, Ceramic Experiment Station, Columbus, Ohio.

[3] "Electrical Resistance of Various Insulating Materials at High Temperatures." Rept., No. 53, National Advisory Committee for Aeronautics.

[4] P. H. Brace, "Electrical Resistivity of Porcelain and Magnesia at High Temperatures," *Trans. Amer. Electrochem. Soc.*, **33**, 205 (1918).

[5] E. F. Northrup, "High Temperature Resistivity of Refractories." *Met. Chem. Eng.*, 123 (1914).

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Description of Layout

A diagrammatic sketch of the apparatus is given in Fig. 1. A 640-volt power line was connected to the terminals of the rheostat R_1. (The rheostat "R" in Fig. 1 should be designated as R_1.) The test unit *TU* was placed in the furnace *F*. This unit consisted of two electrodes, three test pieces and a clamp which holds the electrodes and test pieces together. The details and assembly of the test unit and a sketch of the test piece are shown in Fig. 2. This unit was patterned after the one used by Henry,[7] but instead of a graphite clamp and graphite contacts a nichrome clamp and nichrome contacts were used. The test circuit includes the test unit, *TU*, the single pole double throw switch, *W*, and high resistance voltmeter, *VM*, and the rheostat, R_1. It will be noted that the test set includes three circuits: (1) the line circuit which includes the line switch *S* and the rheostat R_1; (2) the test unit circuit described above, and (3) the shunt circuit which included the voltmeter and the switch, *W*. This latter circuit is used for getting the line voltage and for the most important readings is only employed when the resistance of the rheostat R_1 is entirely in the circuit.

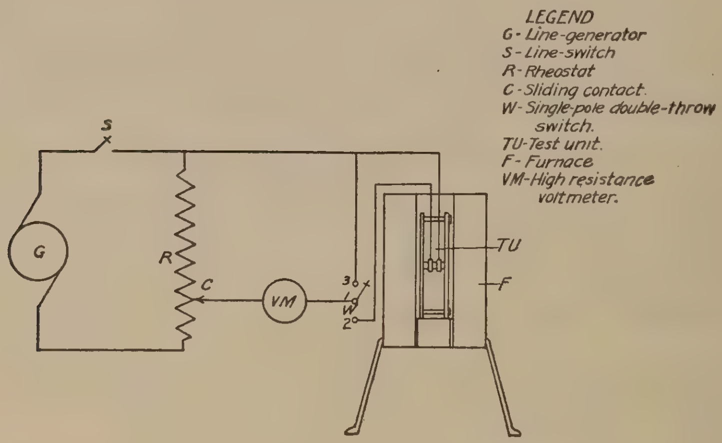

FIG. 1.

In addition to the above described circuits there are two others: (1) the furnace circuit which included the furnace, a controlling rheostat, and a 110-volt feed line and (2) the temperature measuring circuit which consisted of a chromel alumel thermocouple of No. 14 B & S gage wire, a Leeds and Northrup potentiometer, and a thermos bottle cold junction.

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[1] *Loc. cit.*

Description of Equipment

The Power Line This is a plant supply line rated at 625 volts but which often registered as high as 660 volts and averaged about 640 volts.

The Line Switch This is a three pole single throw switch of the enclosed type.

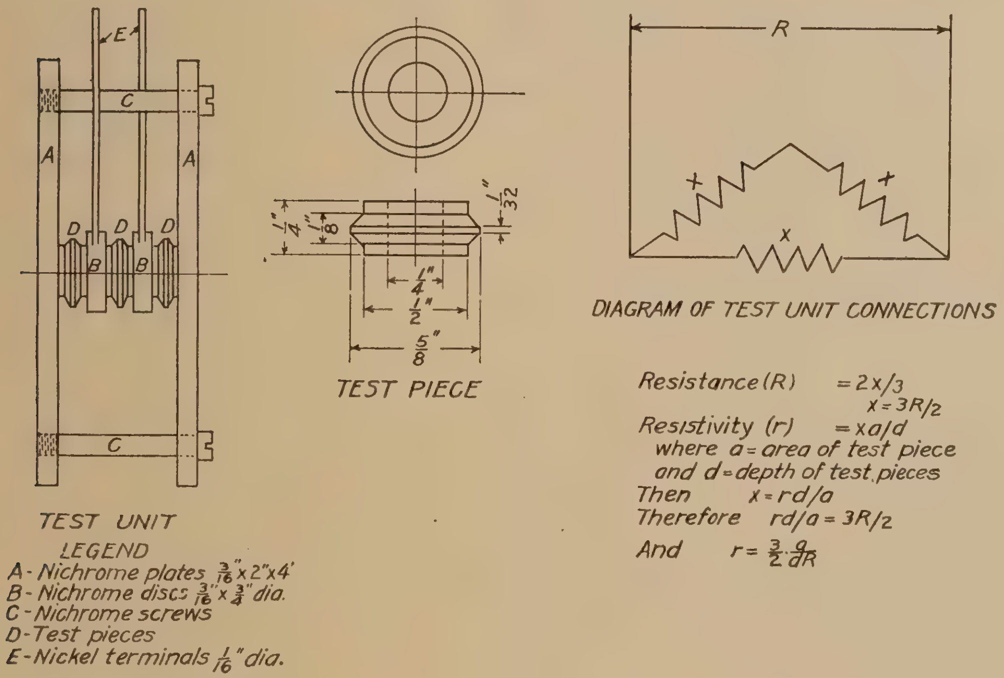
E
C
A
A
D
D
D
B
B
C
TEST UNIT
LEGEND
A - Nichrome plates $\frac{3}{16}$" x 2" x 4'
B - Nichrome discs $\frac{3}{16}$" x $\frac{3}{4}$" dia.
C - Nichrome screws
D - Test pieces
E - Nickel terminals $\frac{1}{16}$" dia.
$\frac{1}{4}$"
$\frac{1}{8}$"
$\frac{1}{32}$"
$\frac{1}{4}$"
$\frac{1}{2}$"
$\frac{5}{8}$"
TEST PIECE
R
+
+
x
DIAGRAM OF TEST UNIT CONNECTIONS
Resistance (R) $= 2x/3$
$x = 3R/2$
Resistivity (r) $= xa/d$
where a = area of test piece
and d = depth of test pieces
Then $x = rd/a$
Therefore $rd/a = 3R/2$
And $r = \frac{3}{2} \cdot \frac{a}{dR}$

FIG. 2.

The Rheostat A laboratory rheostat of the wire wound tube type was used. It has a maximum resistance of 2870 ohms and a maximum current carrying capacity of 0.38 amperes.

The Voltmeter This was the only instrument used in this method for the determination of electrical resistance of the materials tested. This instrument was of the alternating current type having a resistance of 12,800 ohms and a negligible reactance. Alternating current was used in these measurements to obviate, as much as possible, irregularities caused by polarization when direct current was used.

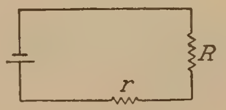

FIG. 3.

The Furnace and Test Unit The unit has been described above. Figure 4 shows the details of the furnace construction.

Routine Procedure for Making a Resistance Test

Ohm's law states that the current passing through a circuit is proportional to the voltage applied and to the resistance of the circuit. The relation is

$E = RI$

when E = the voltage applied

R = resistance of the circuit

I = the current flowing

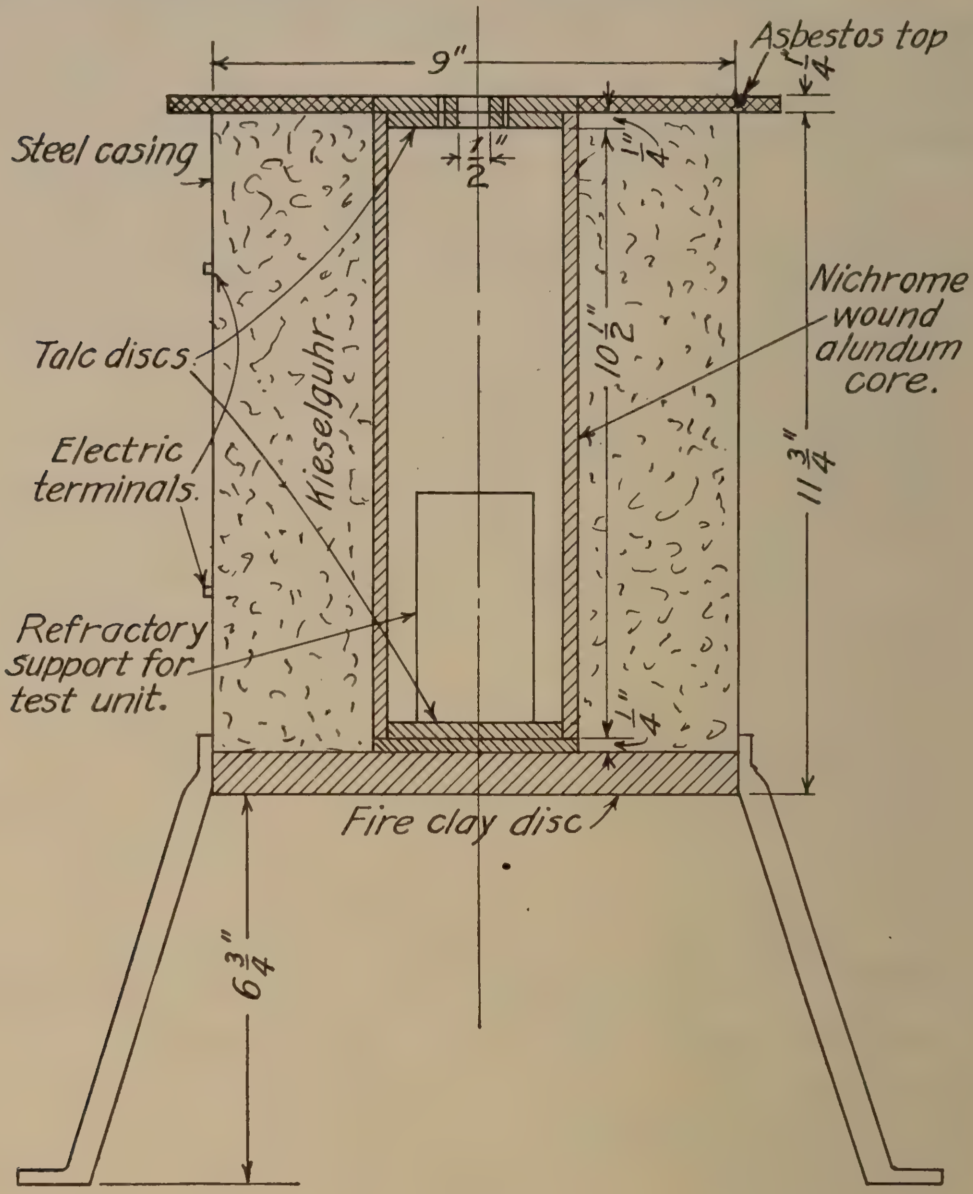

FIG. 4.

If according to the diagram shown in Fig. 3 we have a known resistance, r, placed in series with an unknown resistance, R, then if we apply a known voltage, V, by measuring the voltage drop, V_1, across r it is possible to calculate the resistance, R, as follows:

Let the voltage drop across R be V_2

$$V_1 = r \times I_r$$

$$V_2 = R \times I_R$$

But, $I_r = I_R$

Then, $\frac{V_1}{r} = \frac{V_2}{R}$

Now, $V_2 = V - V_1$

Hence, $\frac{V_1}{r} = \frac{V - V_1}{R}$

V and V_1 can be measured with the voltmeter and r is known. Hence the only unknown in the above equation is R. In referring to the diagram of the measuring circuit (Fig. 1) we have: V equals the line voltage measured by the voltmeter when the resistance of the rheostat R_1 is entirely in and the switch, S, occupies the position 1–3. The resistance, r, is that of the voltmeter which was accurately calibrated. V_1 is the voltage drop across r. R in Fig. 3 represents the resistance of the test piece. The readings were usually taken as follows: The test pieces were heated to the desired temperature. The switch, S, was thrown in and the switch, W, was thrown to the position 1–2. The sliding contact, C, was moved so that the resistance was gradually increased. When the voltmeter indicated the slightest deflection the switch, W, was thrown to the position 1–3 and a reading of the line voltage was taken. This is the voltage at which leakage begins. This data is important in some cases but is difficult to obtain accurately. The switch, W, was returned to the position 1–2 and the resistance increased until the full line voltage was applied to the test circuit. The voltmeter reading was then taken, the switch thrown to position 1–3 and a reading of the line voltage taken. The switch, S, was not allowed to remain closed except when readings were being taken as this causes undue heating of the rheostat. Since three test pieces are used in the test unit the resistance of one test piece is 1.5 times the resistance of the unit. This will be evident from the diagram and calculations shown in Fig. 2.

Accuracy of the Method

The voltage at which the greatest accuracy is obtained is the full line voltage. When the sliding contact of the rheostat is in such a position that the full line voltage is used a slight error will be introduced. Another factor in the accuracy of this method is the position on the voltmeter scale at which a reading is taken. The design of the A. C. voltmeter is such that the scale divisions at the low voltage end are much smaller for a given voltage than at the middle of the scale. For instance, the amount of the scale representing the first fifty volts is about the same as that representing ten volts at the middle of the scale. A third factor in the accuracy is the efficiency of the contacts between the metal terminals and the test pieces. It is extremely difficult to secure a satisfactory contact between refractory test pieces and the metal terminals without using some powdered material which is, in itself, a conductor. Lampblack is about the only conducting material sufficiently fine to use for this purpose and it could not be used for reasons previously given. However, by carefully grinding the faces of the test pieces on an emery wheel an accuracy of ±15% may be obtained when the conductivity is high enough so that an accurate

TABLE I

ELECTRICAL RESISTIVITY OF SOME CERAMIC BODIES AND MATERIALS
(Values given in ohms per Cm^3, 000 omitted)

Body of material	Firing temperature	713°C	739°C	762°C	787°C	812°C	837°C	862°C	887°C	913°C	940°C	963°C	990°C
Chemical porcelain	C13	84	81	81	84	83	80	72	60	46	38	28	22
Bur. Stand. No. 152	C16	548	434	380	356	312	294	272	266	252	232	250	251
Pressed talc	C11	Inf.	Inf.	Inf.	High	1272	750	460	270	250	250	—	204
Massive talc													
Maryland	1100°C	"	"	"	Inf.	Inf.	Inf.	Inf.	Inf.	High	796	225	167
Italian	"	"	"	"	"	High	793	285	225	165	147	116	89
Indian	"	"	"	"	"	Inf.	Inf.	Inf.	779	457	278	217	150
Chinese	"	"	"	"	"	"	"	"	Inf.	Inf.	Inf.	Inf.	Inf.
Beryl	C11	51	47	34	23	17	17	13	9	9	9	8	—
Spinel	C18	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Slight
Sillimanite	C18	"	1090	659	388	388	308	308	308	308	211	172	124
Cyanite	C18	"	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	High	475	228	104
Andalusite	C18	551	334	551	556	556	265	265	226	200	200	165	138
Dumortierite	C18	193	175	146	146	123	110	107	86	81	70	70	52
Periclase	C18	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.	Inf.

reading can be made on the voltmeter scale. This accuracy figure was obtained by averaging differences for duplicate tests on several different materials.

Table I gives the results obtained.

TABLE II

DESCRIPTION OF BODIES AND MATERIALS USED

Chemical Porcelain

Composition of body	Per cent
N. Car. kaolin	15.00
Fla. kaolin	10.00
Tenn. ball clay, No. 5	25.00
Calcined kaolin	20.00
Flint	10.00
Canadian potash feldspar	20.00

Bureau of Standards Body No. 152

Composition of Body	Per cent
Ga. kaolin	10.00
Fla. kaolin	10.00
N. Car. kaolin	10.00
Del. kaolin	10.00
Calcine No. 19	40.00
Calcine No. 14	20.00
	100.00 mature C 16

Calcine No. 19

Composition	Per cent
Kaolin	70.20
Calcined Al_2O_3	27.80
Boric acid	2.00
	100.00 cal. at cone 20

Calcine No. 14

Composition	Per cent
Magnesium Carbonate	18.20
Flint	25.80
Kaolin	56.00
	100.00

Pressed Talc This talc was a California product, almost pure, and closely approximated a theoretical composition. A 300-mesh powder was mixed with linseed oil and pressed into test pieces in a steel die with a standard screw press. The test pieces were fired to cone 11. Talc has the composition represented by the formula $3MgO \cdot 4SiO_2 \cdot H_2O$.

Massive Talcs These talcs were of the physically uniform variety used in making machined talc insulation. The region producing each variety is specified.

Beryl This mineral was the commercial product and contained 11 to 12% beryllium oxide. The formula of beryl is $3BeO \cdot Al_2O_3 \cdot 6SiO_2$.

Magnesia Spinel Magnesia spinel has the formula of $MgO \cdot Al_2O_3$. The material used in making these tests was the electric furnace product and had the following composition: Al_2O_3 72.95, Fe_2O_3 0.25, SiO_2 0.55, and MgO 27.78, a total of 101.53.

Sillimanite The material used was from a deposit in India. An analysis gives: Al_2O_3 62.40, SiO_2 32.29, FeO 2.14, TiO_2 2.10, and loss on ignition a total of 99.85.

Andalusite This material was furnished by Mr. Riddle of the Champion Spark Plug Company and came from a deposit in California. A typical analysis of this material is: Al_2O_3 55.78, SiO_2 35.06, Fe_2O_3, 94, TiO_2 1.64, and loss on ignition 5.76.

Cyanite This material was obtained from the Virginia deposits near Charlotte Court House and had the following analysis: Ignition 0.41, SiO_2 37.28, Al_2O_3 59.93, Fe_2O_3 0.73, and TiO_2 1.20. The formula of the above three minerals is $Al_2O_3 \cdot SiO_2$.

Conclusions

Of the three minerals, cyanite, sillimanite, and andalusite, which have become noted for the formation of mullite in ceramic bodies, the cyanite sample tested seemed to be the best in electrical resistance, with sillimanite and andalusite next in order. This may have been due in part to the purity of the material.

Magnesia spinel has a higher resistance than any one of the three above minerals, and higher than any material tested except the Chinese talc and periclase.

All talcs tested have a higher resistance than either sillimanite or andalusite, but only one talc showed a resistance higher than cyanite.

It seems reasonable to conclude from this data that if we take the composition $Al_2O_3 \cdot SiO_2$ as a starting point and substitute MgO for either Al_2O_3 or SiO_2 the electrical resistance will increase, as the MgO content increases.

A NEW GLASS STONE: $Na_2O \cdot 3CaO \cdot 6SiO_2$[1]

By Albert B. Peck

ABSTRACT

Attention is called to a stone of different composition than any heretofore recorded, and but recently possible of identification by petrographic-microscopic means through the work by Bowen and Morey on the system Na_2SiO_3–$CaSiO_3$–SiO_2. Various ways by which attempts were made to determine the composition of the crystals are described and a summary of the optical properties of these crystals from three sources is given. Probable places for the formation of these stones in the tank are also indicated.

Several years ago the writer received a glass stone for petrographic identification, the optical properties of which proved to coincide with those of no compound previously described in Bowen's[2] very complete description of such phenomena. Hoping that Dr. Bowen might have some later information on the subject, the stone was sent to him and the first negative result was confirmed.

In an attempt to gain some indication of its composition, the finely-ground mixture of crystals and glass was treated with various acids. Sulphuric acid had no effect upon either the crystals or glass. Nitric acid decomposed both the crystals and glass, leaving a skeleton presumably of SiO_2 in place of the crystals. Hydrochloric acid decomposed the crystals, again leaving a skeleton of SiO_2, and hydrofluoric acid dissolved both the crystals and glass. Since ordinary analysis would give the total composition of the crystals and glass combined, which would be the same as that of the undevitrified glass, the solution obtained by leaching the crystals with hydrochloric acid was analyzed and the ratios of the principal oxides present were determined as follows: $CaO:Na_2O = 2:1$ and $SiO_2:CaO+Na_2O = 1.8$.[3] Although microscopic examination showed very conclusively that the crystals were not completely dissolved, the composition of the solution further confirmed the fact that they represented an entirely new type of glass stone. But since no data were available on the ternary compounds of Na_2O, CaO, and SiO_2, the exact identity of these crystals still remained clouded, and owing to the lack of definite chemical information concerning the crystals in question, publication of all data concerning them was withheld.

A few years later Bowen[4] was lead to suspect that these crystals might be the same as those of the natural mineral rivaite, the composition of which had been given as $(Na_2, Ca)Si_2O_5$. Examination of the original rivaite proved that it was in reality only wollastonite embedded in a glass, a condition quite common for glass stones. This disproved rivaite as a distinct species. Further examination of some synthetic "rivaite" showed that it in turn consisted of a glass in which were embedded some crystals similar in optical properties to those of the hitherto unidentifiable glass stone, but the presence of considerable glass in the synthetic "rivaite" still left the true composition of the crystals in doubt.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Glass Division.)

[2] *Jour. Amer. Ceram. Soc.*, **1**, 594–605 (1918).

[3] Private communication.

[4] *Amer. Mineralogist*, **7**, 64–66 (1922).

Soon after this, Insley[1] sent the writer a stone which apparently contained the same unknown crystals but in addition they appeared to be mixed with two other materials, perhaps some partly decomposed sodium carbonate and calcium carbonate. The stone effervesced with hydrochloric acid, and decomposed and became chalky upon short exposure to the air. The writer's stone is still perfectly fresh after years of exposure to the air. Insley reported his stone to have been found in the dead corners of a tank. Soon thereafter, in a description of various stones in glass, Insley[2] recorded the optical properties of these crystals, which were essentially the same as those for the original crystals noted by the writer. Insley described them simply as a sodium calcium silicate.

At a still later date the writer again attempted to obtain the composition of these crystals by leaching the powdered mixture of crystals embedded in glass with hydrochloric acid and later dissolving the remaining siliceous skeleton of the crystals with sodium hydroxide. This method gave the proportions of the constituents as $2Na_2O \cdot 3CaO \cdot 9SiO_2$, but it was clearly evident that all of the skeleton of silica had not been dissolved by the alkali.

Recently Morey and Bowen have published their findings for the system Na_2SiO_3–$CaSiO_3$–SiO_2.[3] In this system they found a compound $Na_2O \cdot 3CaO \cdot 6SiO_2$, which corresponded closely to the crystals found in the original glass stone. They have called attention to this in their paper. The crystals are long and slender, and have a positive optical elongation. Those noted by the writer were always diamond shaped in cross-section, which with the parallel extinction would indicate orthorhombic crystallization, to which they have been assigned by Morey and Bowen. Insley, and Morey and Bowen, also mention hexagonal and octagonal cross-sections. The optical properties from the different sources follow.

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[1] Private Communication.

[2] *Jour. Amer. Ceram. Soc.*, **7**, 14–18 (1924).

[3] *Jour. Soc. Glass Tech.*, **9**, 226–65 (1925).

	Peck	Insley	Morey and Bowen
α	1.565	1.562	1.564
β	1.570		1.570
γ	1.580	1.577	1.579
Optical sign	positive	positive	positive
Elongation	γ	γ	γ
Optic angle (2V)	large about 65°		75°
Crystallization	orthorhombic?		orthorhombic

The stones in the possession of the writer occur as nodules up to two inches or slightly greater in diameter, surrounded by clear glass. They have very much the appearance of wollastonite stones and are true devitrification products. The stones were first found in the sheets as they were drawn from the tank.

Morey and Bowen point out that the crystals forming these stones, as well as those of most other compounds of Na_2O-CaO-SiO_2, are rather unstable and exist without dissociation only through a small range of temperature. Hence, they will be formed only under very specialized conditions. Furthermore, the compound $Na_2O \cdot 3CaO \cdot 6SiO_2$ has a decomposition point of only 1047°C, the lowest decomposition or melting point of any of the compounds in the system, although it may exist in pure Na_2O-CaO-SiO_2 mixtures as low as 725°C. The presence of Insley's crystals in the dead corners of a tank is suggestive in this connection.

The stone described in this paper was probably due to some other cooling influences. As these accumulations were freed either mechanically or naturally, stones would appear in the sheets. A higher temperature in the drawing chamber, perhaps only very slightly greater on account of the low dissociation point of this compound ($Na_2O \cdot 3CaO \cdot 6SiO_2$), would probably eliminate the diffiulty.

Thus another "trouble maker" has been added to the list of glass stones which may be identified by petrographic-microscopic methods, and with its identification assured, correctives for its elimination when it occurs can be applied. This study shows how elusive is the identity of some of these compounds until exact physical-chemical and petrographic-microscopic methods are brought to bear upon them.

The writer here wishes to express his thanks to Dr. Bowen and to Dr. Insley, both of whom have furnished information making this note possible, and especially to Wilbur F. Brown of the Libbey-Owens Sheet Glass Company from whom the original stones were obtained.

Mineralogical Laboratory
University of Michigan,
Ann Arbor, Mich.

A MODERN SEWER PIPE PLANT[1]

By W. D. Richardson

ABSTRACT

A sewer pipe plant design including radical departures from plants in operation now is described. Tunnel driers of special design are suggested as most practical. Salt glazing in continuous kilns, using gas or oil as fuel, is discussed. A feeder for introducing the salt into the kiln is described.

Last year I was engaged to test the clays that were available and make an estimate of the cost of a one-press sewer pipe plant. In this investigation the plants that had been most recently built and the drawings of one that was then being built were examined. I found that in the past twenty years or more very little change or improvement had been made in the style or arrangement of sewer pipe plants, and that practically no economies in the manufacture had been introduced. A few improvements had been made in machinery, but there was the same large three or four story building for drying and finishing the pipe and the same round downdraft kilns for firing them. The

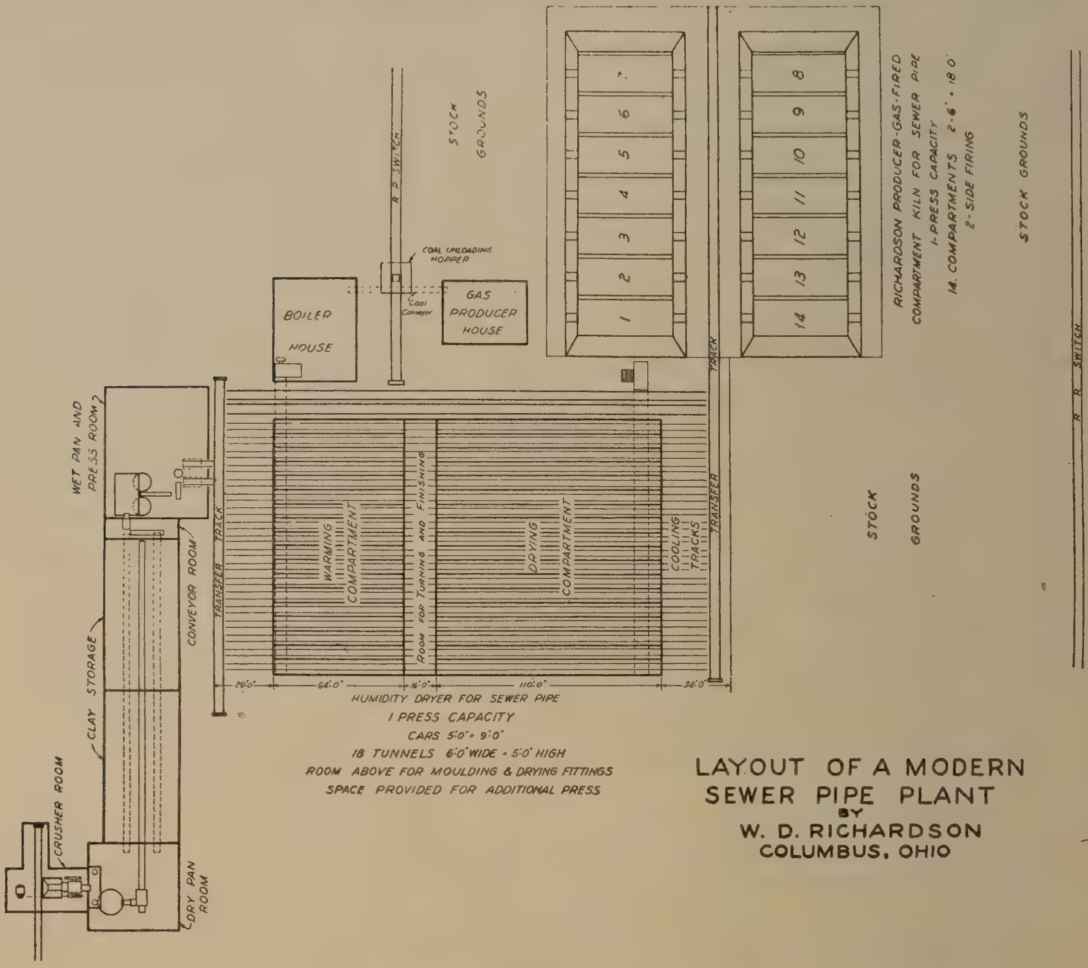

Fig. 1.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Heavy Clay Products Division.)

expense of handling and storing so many pipe in the process of drying and the waste of fuel in firing set me to giving more thought to the possibilities of correcting these deficiencies than the occasion really demanded, since the project of my clients had not yet been capitalized and I had no contract for further engineering service. However, I was sufficiently interested to make a preliminary layout of a plant embodying some rather radical changes, especially in the equipment for drying and firing of the pipe.

I am pleased to bring before the Heavy Clay Products Division of our SOCIETY my idea of a modern sewer pipe plant, soliciting your criticism. The pictures will show the general arrangement of the plant and will enable me to describe the special features. I have gone over the design many times, and have sketched the details of the drier, the only feature that is, in part, new to me, though I have not taken time to make working drawings of it.

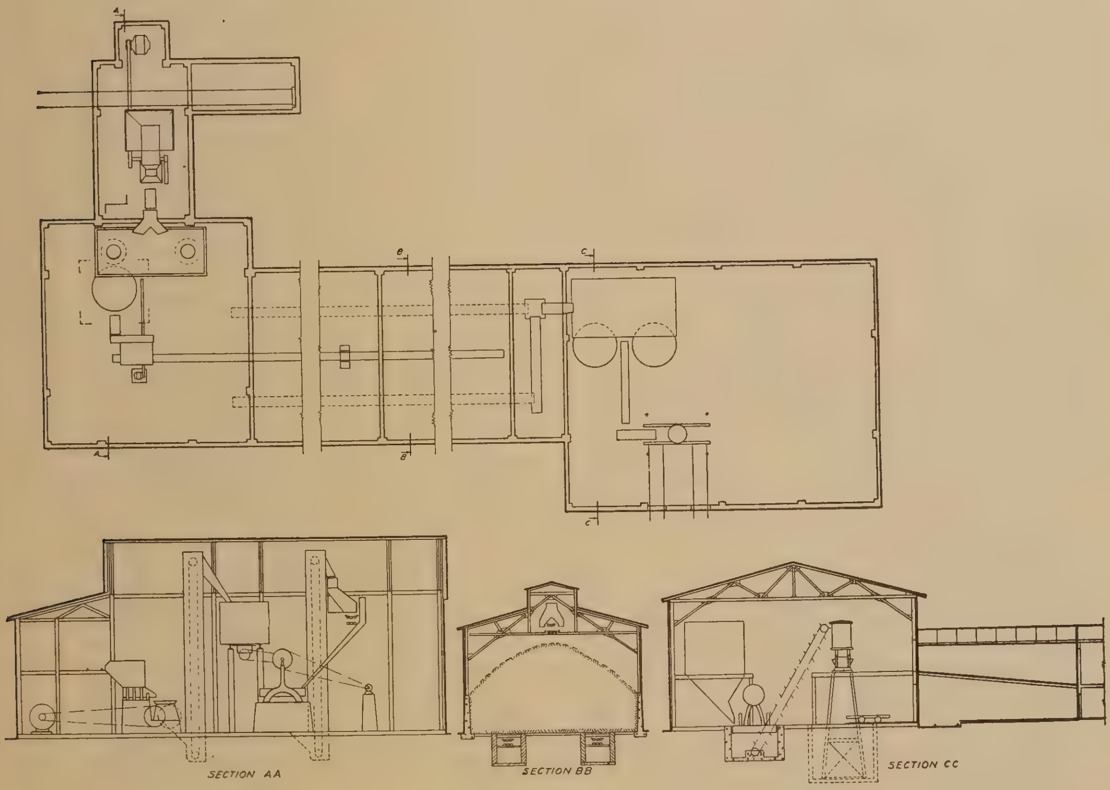


FIG. 2.

Clay Preparation and Storage The clay preparing and clay storage features are such as we commonly make for many heavy clay products plants. The main purpose of the design of storing the clay, ground and screened, is to secure a homogeneous body of uniform composition from hour to hour, day to day, and month to month throughout the year. All clay formations vary more or less from top to bottom of the deposit and it is practically impossible to mix thoroughly the different strata in mining. The storing of raw clay as it comes from the mine, or even of crushed clay, does little good. Clays can only be well mixed when they are in a finely pulverized condition and uniformity can only be secured by storing the pulverized clay in bins 15 to 20 feet high. In this way the variations in the clay as mined are evenly distributed over the bin by an automatically traveling tripper on a troughing belt conveyor. With a long enough and high enough pile, fed down onto a reclaiming conveyor underneath the bin, a uniform material is obtained. By this uniformity of material and homogeneity of the body of the ware we have many times overcome defects that were thought to be due to improper drying or firing.

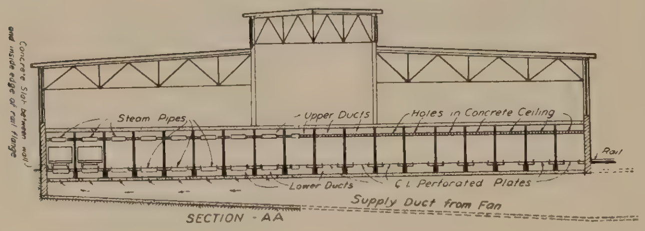


Fig. 3A.

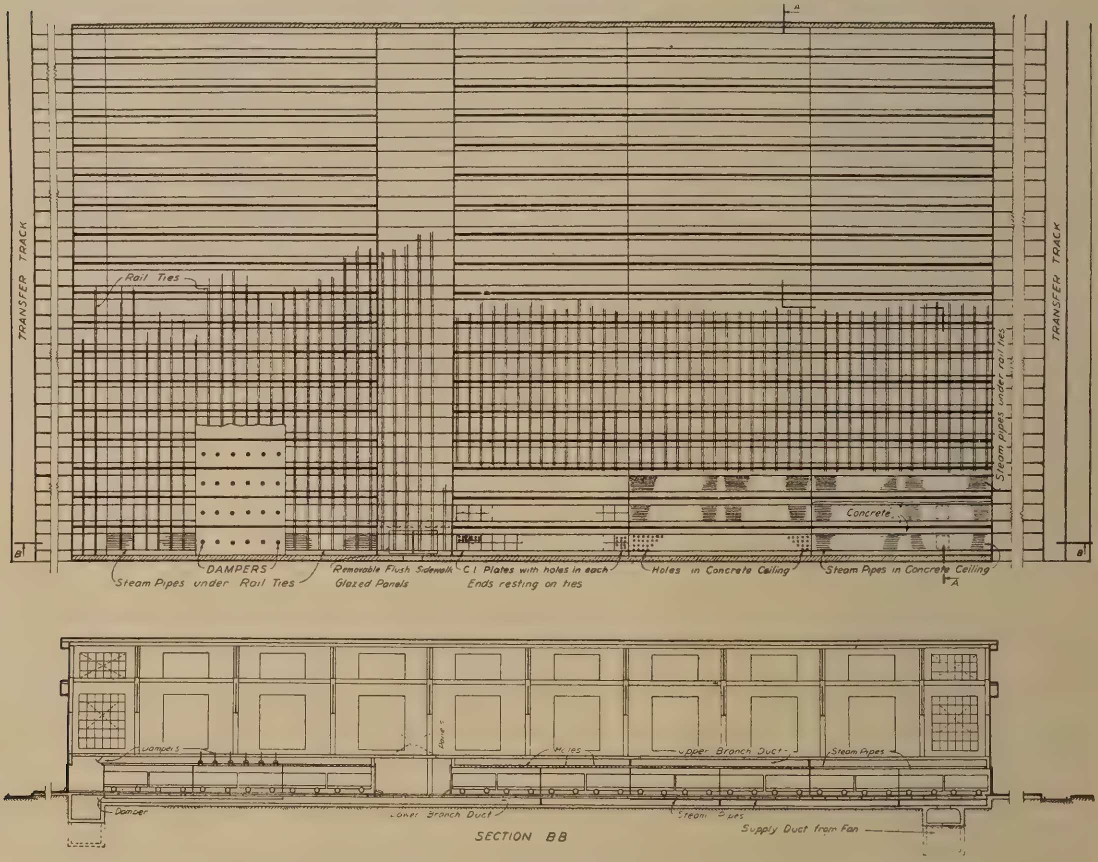
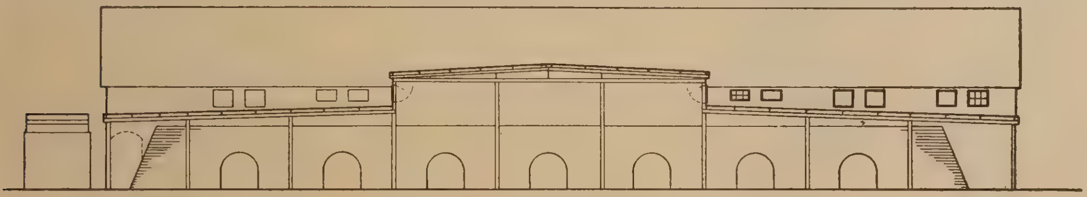

TRANSFER TRACK
Rail Ties
Steam pipes under rail ties
Concrete
TRANSFER TRACK
B
B
A
DAMPERS
Steam Pipes under Rail Ties
Removable Flush Sidewalk Glazed Panels
C. I. Plates with holes in each Ends resting on ties
Holes in Concrete Ceiling
Steam Pipes in Concrete Ceiling
A
Dampers
Holes
Upper Branch Duct
Steam Pipes
Damper
Lower Branch Duct
Steam Pipes
Supply Duct from Fan
SECTION BB

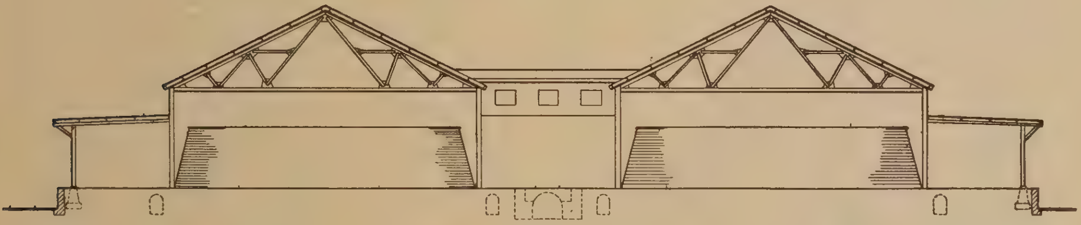
Fig. 3B.

A secondary advantage of ample clay storage is no delay in manufacture due to interruption in mining or preparation operations.

Drying The drying of sewer pipe on cars in a tunnel drier is not new. I saw such a plant more than twenty years ago. I do not know whether it is in operation today, but if it is, the drier has doubtless been much improved, though it was apparently successful at that time. We have learned a good deal about drying clay products since then and we now know that in a closed room, the space around the ware being comparatively small, where the temperature, the humidity, and the circulation are under control, the most elaborately molded clay bodies can be dried in a fraction of the time that they were formerly dried in working or drying rooms and with less damage to the ware. Why should not sewer pipe manufacturers take advantage of this?



LONGITUDINAL SECTION BETWEEN KILNS



CROSS SECTION THRU KILN BUILDINGS

FIG. 4.

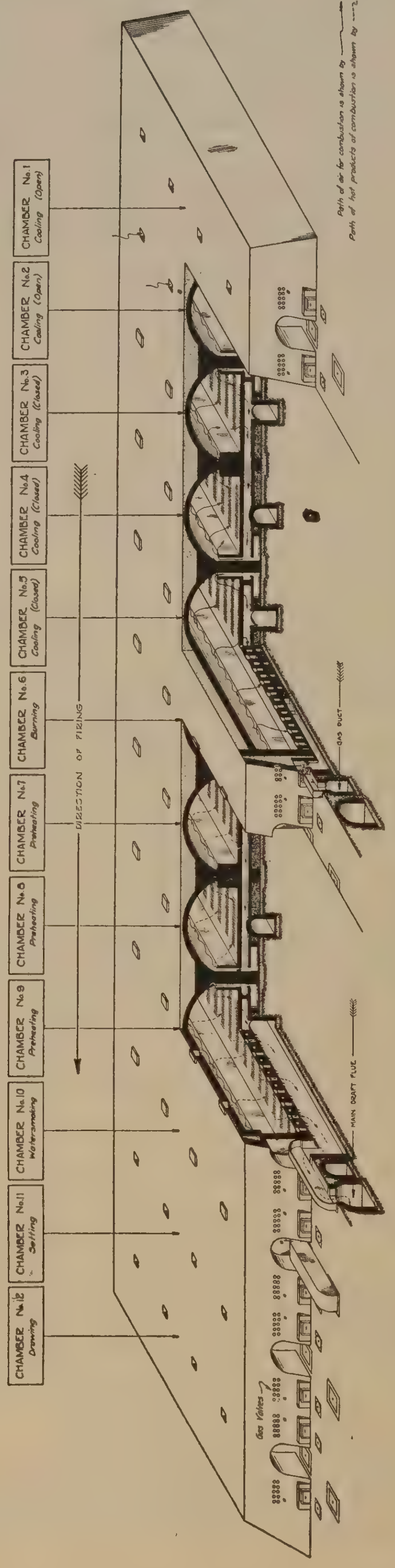
Why build such strong high buildings with so little of the cubic contents utilized and be obliged to provide space for carrying pipe so long in the process of drying? Of course, a certain amount of various sizes of dry pipe must be available for setting kilns to advantage, but probably with proper planning, such stock need not be so excessive and could be carried on cars in tunnels at small cost. Fittings are molded, dried and stored in a room over the tunnel drier from which they can be taken to kilns as required.

The cars I have in mind for this plant have a perforated steel platform 6 x 9 feet, the platform being level with the floor of the press room. Such a car would hold six 24-inch pipes, and could be pushed by one man into drier and from drier onto transfer car and from transfer car into kiln. The cars would, of course, be moved through the drier by power in a simple manner.

There are two permanent compartments in the drier, the first for warming and preliminary drying to a "leather hard" condition for finishing the larger sizes of pipe; the second compartment is for rapidly drying the pipe by progressing them gradually through sections of increasing temperature and decreasing humidity. For this I have used my compartment tunnel drier, the tunnels being divided into compartments for up-and-down draft circulation by means of steel plate baffles on the rear of every other car, fitting rather closely to the sides and to the top and bottom of the tunnel and forming movable partitions in the tunnel that force alternately the desired up-and-down movement of the air through the pipes and prevent the longitudinal circulation over the top, under the bottom and around the sides of the cars as is usual in tunnel driers.

Between the two permanent compartments of the drier is a room for finishing or turning the larger sizes of pipe on the cars. In this room there are, over each track, trap doors in the top that are easily opened for light and ventilation when finishing pipe or moving cars from the first to the second compartment, but which at other times are closed down for a passage way on the floor of the fittings room above.

It is designed that two cars at a time be moved through the tunnel. Only one of these cars will be in the finishing room at a time. By placing two cars in the tunnels and taking two cars out of the tunnels there will


CHAMBER No.1 Cooling (Open)
CHAMBER No.2 Cooling (Open)
CHAMBER No.3 Cooling (Closed)
CHAMBER No.4 Cooling (Closed)
CHAMBER No.5 Cooling (Closed)
CHAMBER No.6 Burning
CHAMBER No.7 Preheating
CHAMBER No.8 Preheating
CHAMBER No.9 Preheating
CHAMBER No.10 Watersmoking
CHAMBER No.11 Setting
CHAMBER No.12 Drawing
DIRECTION OF FIRING
GAS DUCT
MAIN DRAFT FLUE
Gas Valves
Path of air for combustion is shown by
Path of hot products of combustion is shown by

COMPARTMENT TYPE RICHARDSON CONTINUOUS KILN FOR PRODUCER GAS

FIG. 5.

always be partitions at the same points.

Though the tunnels are heated by steam pipes under the tracks of each tunnel and at top of the tunnel in the last two sections at hot end, yet the circulated air is heated either by a small steam heater or by the heat from a cooling kiln. This heated air is blown into the drier by a fan and distributed in the usual manner. The circulation of the air in the tunnels and the removal of the vapor is by another fan.

In the first, or warming-up compartment of the drier, there is little or no artificial circulation and absolutely none in the first two sections. Circulation of high humidity air is provided in the third section.

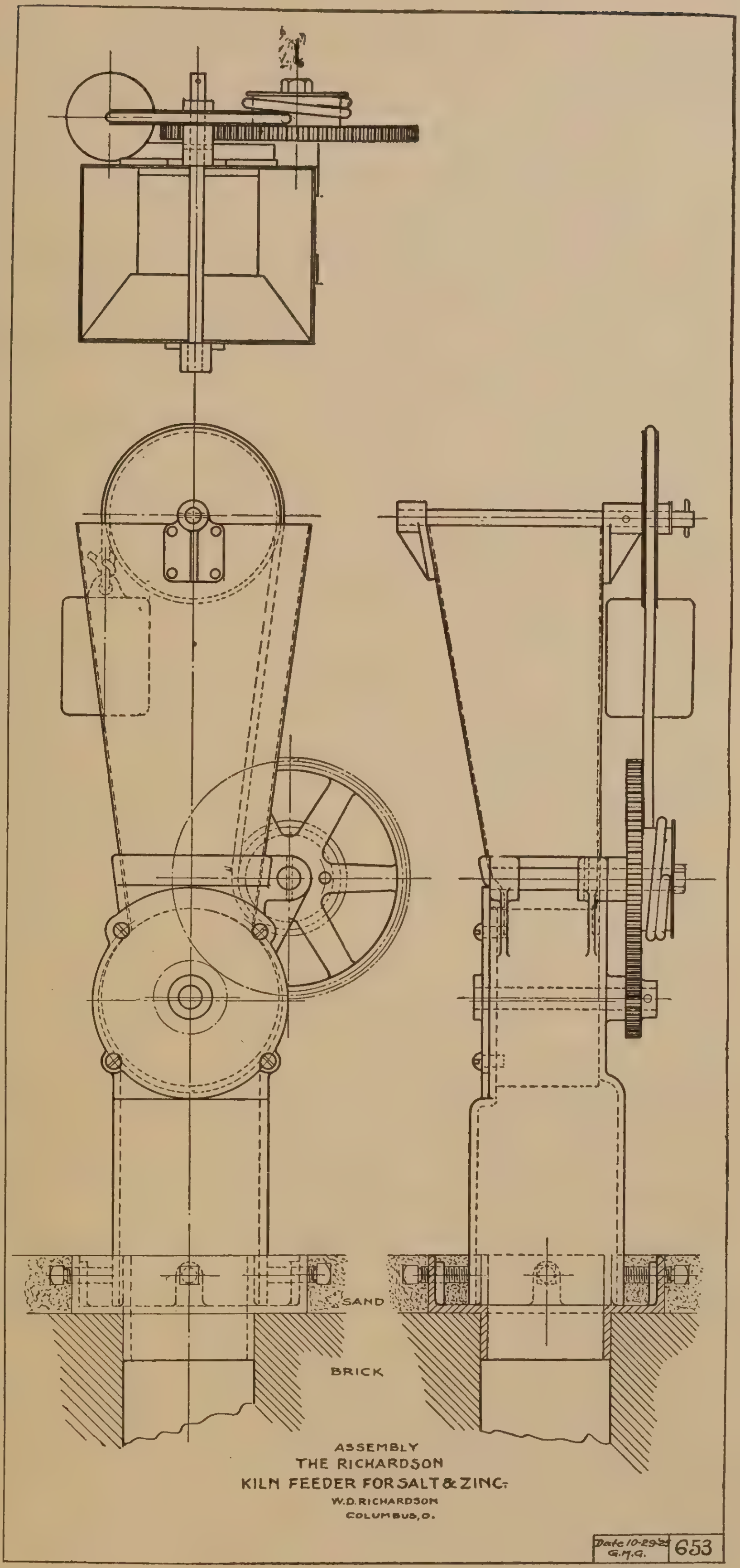


FIG. 6.

The drier can be provided with temperature and humidity controllers.

Transfer The cars of pipe are taken to kilns by the usual electric transfer car, the kiln doors being wide enough to permit of the car passing into the kiln.

Kilns The next radical feature of the modern sewer pipe plant is the kiln, a producer-gas fired compartment kiln, fully regenerative and continuous in operation. The kiln is not new; its present form has been developed through many years of experience with such kilns and has been for a long time in successful operation. The only new and untried thing about the kiln in this country is its use for the firing and salt glazing of sewer pipe.

Salt Glazing in Continuous Kiln We have been asked many times in the past ten or fifteen years if salt glazing could be done in the continuous kiln. We have answered that we could see no reason why it could not be done; that it was being done successfully in Germany. We know of no attempt in America to salt glaze sewer pipe in the continuous kiln nor of any systematic experiments by technical men to do salt glazing in such a kiln, except that Ellis Lovejoy years ago successfully salt-glazed brick in a Guthrie kiln at Union Furnace, Ohio. The making of salt-glazed brick was out of their line and the demand at that time was small, so the production of salt-glazed brick was not continued.

Sewer-pipe men have reasoned that salt glazing could not be done in a continuous kiln because fumes would injure the pipe being preheated. In what way, they could not tell, and when sifted down it has been found to be only an empirical opinion based neither upon theory nor practice.

About two years ago, an unsigned article in the *British Clayworker* stated that

> continuous kilns are not satisfactory because the salt vapors would be carried into a succeeding chamber before the pipes in the latter were ready for salting, and consequently such pipes would be spoiled.

I immediately wrote to the editor asking him to get a specific statement from the writer as to just in what way and why the vapors of the decomposed salt would injure the ware that was being preheated. After waiting two months and receiving no answer I wrote again and finally the editor answered as follows:

> The truth of the matter is that we made some inquiries that were not satisfactory and we have since had to follow these up in quite another direction. We are now in touch with a German firm in the matter and hope in the course of a very short time to be able to give you the information you require.

Though this was in August, 1924, the information has not been received.

I have asked some of our well-known ceramic chemists for their opinion on this matter and all state that they do not think the salt vapors passing out of the compartment under fire would have injurious effect on the ware being preheated.

Salt Glazing with Oil or Gas

Sewer-pipe men have said that salt glazing could not be done with gas or oil, but no finer salt-glazed sewer pipe are made anywhere than those in Ohio fired with natural gas. Of course, there is no reason why this should not be so. They could be fired also with producer gas.

I have a clipping from the *Tonindustrie Zeitung*, No. 73, 1912, which states:

> The best results for firing of sewer pipe in continuous kilns have been obtained in the ones which are gas-fired. Such kilns have also been used for stone ware. The regulation of the firing has no difficulties, and it can be fired either oxidizing or reducing. The salting is done from the top of the kiln, through properly constructed holes, and the sewer pipe have always shown as good glaze in the bottom as on top. It is claimed that such gas-fired continuous kilns have produced 96% first-class sewer pipe.

Salt Glazing in Continuous Chamber Kilns

H. G. Schurect secured information through technical journals which was mostly to the effect that though there was a saving in fuel in the continuous kilns the glaze was not as good as that produced in intermittent kilns. I have looked up these references in the *Tonindustrie-Zeitung* and in *Keramische Rundschau.* These answers are to the effect that salt glazing is done successfully in such gas fired compartment kilns but it is necessary that the kiln be so constructed that during the salting the compartment can be disconnected from the other compartments and closed tightly with dampers when required. I am convinced that the kilns we are now building are superior for salt glazing.

For feeding the salt into the kiln in a continuous stream as fast as it will volatilize, I have devised a small automatic feeder, geared and operated by a weight that will feed a charge of salt as slowly as may be desired. If thought best fine coal may be mixed with the salt in the charge. With this apparatus feeding in this manner, it is believed that quicker and better results will be obtained, as the salting will not cool down the kiln and the temperature and kiln atmosphere are under instant control by valves.

Salt Glazing in Car Tunnel Kiln

I have also a car tunnel kiln that I believe is better adapted for firing sewer pipe but I consider the tunnel kiln more of an experiment and hesitate to take the responsibility of recommending it. The compartment kiln, however, is safe, reliable, flexible, and economical.

Schultz Bldg.
Columbus, Ohio

E-90-P COMPARATIVE TEST OF HAMMER MILL PULVERIZER AND DRY PAN FOR CRUSHING STREATOR SHALE[1]

By D. P. Ogden

ABSTRACT

In the machines as described below the following points are discussed: (1) the grinding action, (2) energy consumption per ton ground, (3) capacity to produce fines six-mesh and under, (4) to determine the operating characteristics of the hammer mill. The conclusions given are: (1) The dry pan will not grind shale chunks larger than 15 inches maximum diameter, nor chert nodules of any size. The hammer mill grinds easily in one operation all chunks small enough to go through the 20x42-inch hopper opening and all chert nodules. (2) The energy consumption of the dry pan as compared to the hammer mill in kw. hrs. per ton of fines through six-mesh is approximately as 1.40 to 1.25. (3) The maximum capacity of the Frost 9-foot dry pan with $\frac{1}{4}$-inch screen plate openings was known to be approximately 25 tons through six-mesh per hour. The maximum capacity of the 30x42-inch Williams hammer mill as reached in these tests with hand feeding was found to be 56 tons total feed and 42 tons through six-mesh per hour. This figure could have been greatly exceeded if the material could have been fed more rapidly. The dry pan tailings coarser than six-mesh compared to the hammer mill tailings of the same coarseness are as 40 to 25%. (4) The hammer mill is more efficient than the dry pan in practically all respects if properly set up and operated, but it is easily possible to secure less efficient results from the hammer mill, particularly if the feeding is not properly regulated.

Introduction

This test was a practical tryout of the hammer mill as a substitute for several dry pans for the grinding of mine-run shale in one operation in the production of shale face brick. The laboratory work was necessary to correlate and compare the performance of the two machines. In all cases the data obtained is from the same shale deposit and was mined under identical conditions and at the same time of the year.

Earlier Test with Pulverizer In 1922 a test was run on the "American Ring Pulverizer" in the plant of the Decatur Brick Company at Decatur, Illinois. The data from this test showed that considerable improvement might be hoped for if the very severe momentary overloads on the motor could be avoided by storing more kinetic energy in the rotating system either: (*a*) by increasing the weight of the fly wheels, (*b*) by increasing the rotational velocity of speed in revolutions per minute of the hammer shaft. Accordingly, when the pulverizer tested was ordered from the manufacturer it was specified to be equipped with two extra heavy fly wheels. Also, this machine was direct connected to a 1200 r.p.m. constant speed induction motor, whereas the machine at Decatur was driven through a belt at a speed of less than 600 r.p.m.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Heavy Clay Products Division). Received March 19, 1926.

The Dry Pan The dry pan was the Frost 9-foot dry pan of the conventional design having screen plate openings approximately $\frac{1}{4}$ inch across. It was operating under its normal production conditions.

The feed was by an inclined belt conveyor running in the bottom of a trough and consisted of mine-run shale, except that hard nigger-heads or chert nodules encountered had to be thrown out by hand, and it was regular practice to split up, by means of a pneumatic air tool, chunks having any dimension greater than 18 inches.

This feeding, for a capacity of approximately 35 tons per hour required the services of two men and an 18-inch wide belt conveyor.

This dry pan was driven from a line shaft which also served a brick machine and miscellaneous auxiliary equipment. In making the energy consumption determinations for the dry pan the idling load of the motor and line shaft were measured by disconnecting all machines from the line shaft. Next, the total load of the line shaft and of the dry pan grinding shale was measured, such that by subtracting the idling load of the line shaft from the total load of the line shaft and dry pan, the energy delivered to the dry pan could be closely approximated. The error in this method, if any, would be such that the total load of the dry pan would be greater than the determination, for the reason that the energy lost in the belt driving the dry pan would be partly charged to the line shaft. The determinations as made, however, were the best that could be had without setting up an individual motor to drive the dry pan, which was virtually out of the question and not considered necessary.

Hammer Mill The hammer mill is described by the maker as a "Williams 30x42 Decksweeper Pulverizer" and in this test was direct connected to a G. E. Co. 1200 r.p.m., 100 h.p. squirrel cage motor.

A temporary timber frame was provided for supporting the hammer mill and motor. Also, a little wooden frame work over which tarpaulins could be pulled to protect the machinery during inclement weather was provided. The motor compensator and meter current transformers were mounted on this wooden frame work. A wooden guard was put around the flexible coupling between the motor and hammer mill so that stray chunks of material which might fall on this rapidly rotating coupling would not be a source of danger by being thrown from it. These details are well shown in Fig. 1.

A charging platform immediately adjacent to and at a slightly lower level than the Streator Brick Company production shale car track was built of heavy planks supported on a timber frame such that this platform could receive mine-run shale dumped from the side of the production rocker dump car. The height of this charging platform was made such that shale pushed over its east edge would fall directly into the hopper of the hammer mill. The intention in this arrangement was to make it as easy as possible to push rapidly, large quantities of shale into the hammer mill hopper. This arrangement worked out only moderately well because of the high capacity of the machine being tested. The procedure in this test was for as many men as could be gotten around a measured pile to push and shovel as fast as they could into the hopper opening of the machine. This arrangement is shown in Fig. 2.

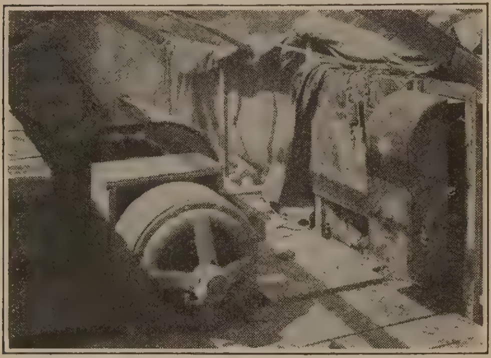

FIG. 1.—Motor and drive end looking north.

Some difficulty was experienced with material flying back out from the hammer through the hopper opening. After the photograph of Fig. 2 was taken a hood was built over this hopper opening and brought up to a vertical wall built of boards. The hopper opening itself was closed off by pieces of 2 x 4 suspended by holes drilled through their top ends, which almost closed the opening leading to the hopper such that it was possible to push the shale to be fed through this swinging wooden curtain, but such that the pieces flying back could not get out. This arrangement was found to work very well indeed, and virtually to eliminate the difficulty from flying pieces. As would be expected this trouble was greatest when hard and flinty material was being fed into the machine.

An ordinary service type watt-hour meter was used to make the determinations of electrical power and energy fed to the motor. By removing the cover of this meter and putting a small mark on the meter disk it is possible to get the time of one revolution of the meter disk by using a stop watch. Thus, this instrument can be used to secure what amounts to an average power determination during the time of one meter disk revolution since a definitely known amount of energy is consumed for each revolution of the meter disk. This time is so short (from 1 to 5 or 6 seconds) that these average power determinations in reality can

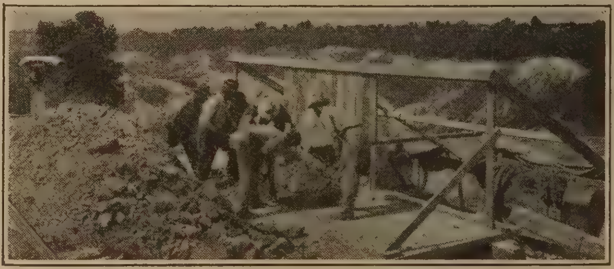

Fig. 2.—Charging platform looking northeast.

be considered as instantaneous maxima. Actually these determinations of maximum demand are much more satisfactory in tests of this nature than the readings of an indicating watt-meter, for the reason that the indicating watt-meter pointer is apt to move so rapidly that it is difficult to read at all. The average power and the total energy consumed during any definite time are at once obtained by merely counting the meter disk revolutions and measuring the number of seconds from the start to the finish of the run. The data that it is necessary to record for these determinations is shown below. The method of mounting this meter is shown in Figs. 2 and 3.

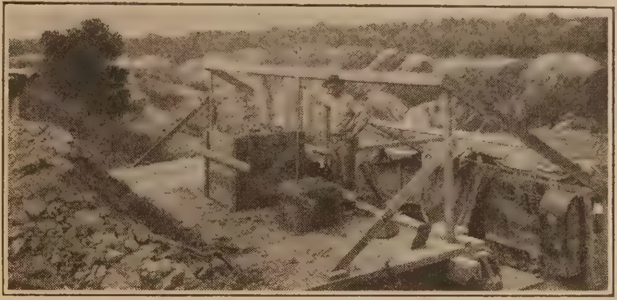

FIG. 3.—Measuring boxes on charging platform.

The weight of shale to be used in each run was greater than the capacity of any scale that could conveniently be moved to the location of the test. Therefore two bottomless boxes were made having capacities of one cubic yard, and one-eighth of one cubic yard respectively. In this way it was possible to fill up both boxes from the same pile of shale for any particular run. These boxes are clearly shown in Fig. 3. Next, the small $\frac{1}{8}$-yard box which had been placed on a steel plate before filling, was picked up and set on a platform scale and the weight of the shale determined. It was assumed that the weight of the large box full of shale was exactly eight times the weight of the smaller box and in this way the weight of the large box full of shale was computed.

FIG. 4.—Discharge of hammer mill looking south.

The timber platform carrying the pulverizer and motor was so constructed that a space approximately eight feet high was left free under the discharge of the hammer mill. Just before each run was started this space was cleared out of the shale that had been previously ground and a clean wheel barrow was put directly under the discharge opening of the machine. Thus, when the run was started, part of the tailings or discharge from the hammer mill went into the wheel barrow. Actually in practically all runs the wheel barrow was entirely buried and had to be dug out. The wheel barrow load was then taken out from under the hammer mill and

TABLE I

E-90-P Tests of Williams 30x42 in., "Decksweeper Pulverizer" directly connected to G. E. Company 100 h. p., 1200 r.p.m. Type KT Motor at Streator (Ill.) Brick Company between 7-1-25 and 9-15-25. Frost 9-ft. Dry Pan Driven from Line Shaft $\frac{1}{4}$-in. Screen Plate Openings.

Run no.	Date	Time in sec.	Meter disk revs.	7 Kw. hrs.	Av. kw.	Shale fed in hopper				
						Kind and siz	Wt. (tons)	Kw.hr. per ton	Sieve test sampleno.	Remarks
1*a*	7-1	79	10	.600	27.5	Mine-run shale	10	1.2	1	2 men shoveling; no large chunks
4	7-3	63	8	.480	26.4	Spoil pile nodules	.35	1.28	4	3 men feeding nods to mach.
5	7-10	50	10	.600	43.2	Mine-run shale			5	
10	7-18	17.3	47	2.82	58.7	Mine-run shale	2.7	1.05	10	6 men feeding machine
16	8-5	76.8	$10\frac{1}{4}$	.10	100.25	Dry pan on mine-run shale		1.41	16	Loaded heavily Production operation
20*a**	8-29	285	20	1.2	15.4	Mine-run shale	1.35	1.12	20*a* 20*b**	These tests were made with *roller out and every other row of hammers out*
26	9-3	100	11	.66	23.7	Mine-run shale with chunks 30 in.	.468	1.4	26*a* 26*b*	Roller back $\frac{1}{2}$ in. (limit) alternate hammers in each row out
29	9-5	36	4	.24	24	Chunks and mine-run shale	.264	.91	29*a*	Roller in, alternate rows of hammers out
	9-5	15	3.5	.21	50.5	Large chunks	.27	1.3	29*b*	Roller in, alternate rows of hammers out
35	9-14	125	11	.66	19	Mine-run shale	.1	6.6	35	1 large chunk
40	9-15	31	$11\frac{3}{4}$	.72	82	Large-chunks and mine-run shale	.5	1.44	40	
41	9-15	195	22	1.32	24	Mine-run shale	.1	1.32	41	Extra wet
42d	9-15	Sample taken from bin over brick machine screened shale							42*d*.	

* Sample 20*a* taken from E side of pit under machine. Sample 20*b* taken from W side of pit under machine during same run as 20*a*. Coarse tailings rebounded from E side of machine to W side of pit.

dumped on a large steel plate. The pile thus made was formed into a cone and quartered in the approved fashion. Diagonally opposite quarters were discarded and a smaller cone was made. In this way the samples were reduced to such size that they could be conveniently put into cardboard cartons to be carried to the sieve test laboratory. In the laboratory a Tyler sample splitter was used to further reduce the samples to approximately 500 to 1000 grams, such that they could be contained in Tyler standard sieves. The discharge opening is shown in Fig. 4. The sieve test data was obtained in the usual way by using a Tyler rotap sieve shaking machine. Determinations were made with screens at each of the following sized openings: 1.050-, .525-, .263- or 3-mesh, 6-, 8-, 10-, 14-, 20-, 28-, 35-, 65-, and 150-mesh.

Data

In this test a total of 41 runs was made. However, many of these runs are not very interesting for the reason that they were made only to teach the men concerned what to do, or to try out some minor change that had been made in the arrangements. The runs shown in Table I are those which correspond to the curves shown and are believed to include the most interesting data of the test.

Summary

The method of securing the above data has been described. Table I shows all the essential data for each run that was secured with the exception of the detailed field notes on the weights of shale as fed, and the weights of each fineness in the sieve tests. Sample 42*d* was taken from the screened shale bin over the Streator Brick Company's brick machine and is included merely for the purpose of comparing the data from the dry pan and hammer mill discharge.

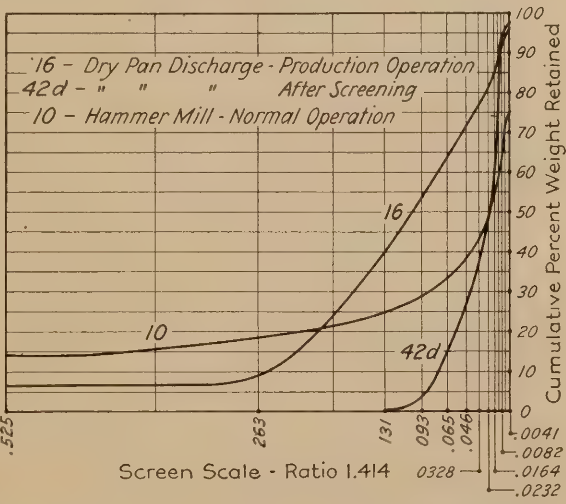

FIG. 5.—E–90–P Test of Williams 30 x 40-inch hammer mill at Streator Brick Co., Streator, Ill.

On all the curves the vertical ordinate corresponds to the per cent of material coarser than the opening corresponding to the abscissa of the same point. If any particular size opening is determined it is easy to see at a glance the amount of material that will pass this opening and the amount that will be retained. It should be understood that these curves are plotted from laboratory sieve tests and that these openings do not correspond to the openings in a production screen. The curve in Fig. 5 shows the marked difference in grinding characteristics between the dry pan and hammer mill. It is possible that the dry pan would give more nearly the same shape of curve as the hammer mill if some way could be devised for instantly removing the fines as fast as they were produced.

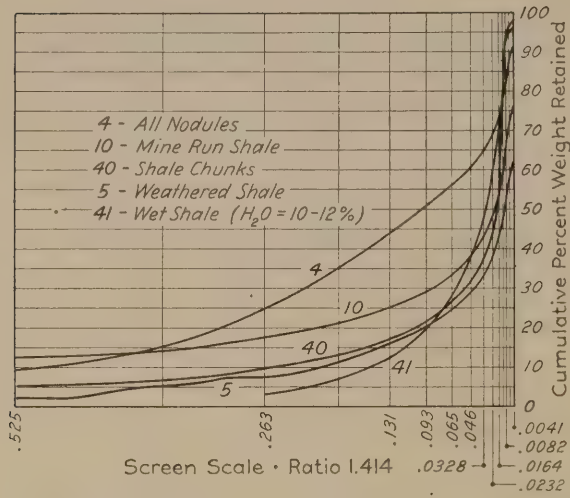

FIG. 6.—All runs from hammer mill.

The curve in Fig. 6 demonstrates the ability of the hammer mill to reduce all sizes of feed in one operation. It can be seen that good grinding performance was obtained on practically all materials that were fed in in these runs.

It is well to mention here that at no time was it possible to feed the machine fast enough to keep the motor even reasonably well loaded; that is, in these tests we were unable to demonstrate the capacity of this machine because of the method used in feeding it. It was hardly practical to set up a mechanical feeder for the purpose of this test.

The curve in Fig. 7 is intended to show the result on the fineness of grinding of removing the hammers. It will be seen that either taking out alternate rows of hammers or taking alternate hammers out of each row considerably increases the coarseness of the discharge. It seemed that the most satisfactory operation was obtained with alternate hammers out of each row, since when all the hammers in alternate rows were removed occasionally very large chunks of material were passed by the machine.

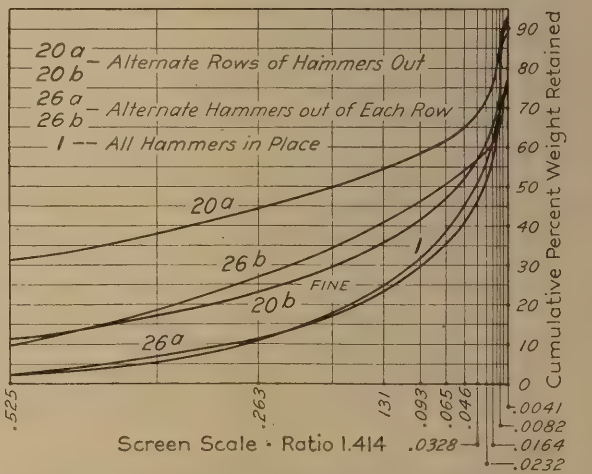

FIG. 7.—All runs from hammer mill.

It was found that with all hammers in, and with the small hammer circle of the machine being tested (30-inch diameter) that very large chunks would not feed down into the machine because the impact between successive hammers was so close together that the chunk was kept in the air. Also, with all hammers in, the fineness of the grinding was greater than was considered necessary and it was thought that a saving in power consumed would result if the grinding was made only as fine as was necessary. These beliefs were all borne out by the data obtained.

The curve in Fig. 8 shows the result on power consumption of improper feeding. The data in run 35 was secured from one large chunk only, and this chunk was bounced around on top of the hammers for a total of 125 seconds. The great length of time and small weight of shale fed accounts for the high power consumption. This condition, of course, is unusual. At the same time if proper precautions are not taken to avoid it, it might easily be encountered in production operation.

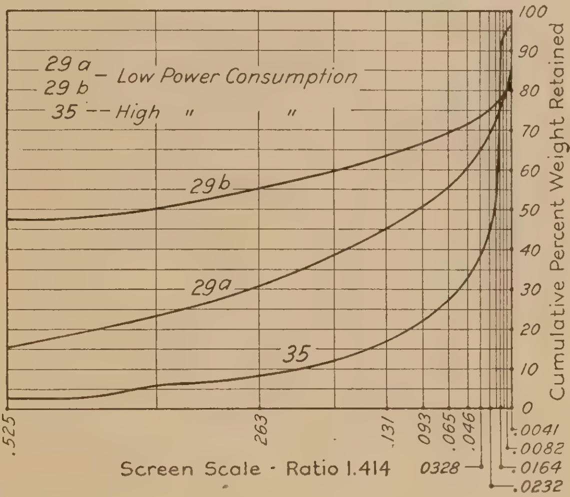

FIG. 8.

Figure 9 was taken looking down into the hopper of the machine tested and shows at the bottom of the picture the breaker roll and grinding plates. In immediate foreground can be seen the hammers and their mountings.

As a result of these tests it has been decided that to grind the large chunks and to secure a capacity sufficient for a production of 200,000 building brick in eight hours that a larger hammer mill than the one tested would be needed and has been provided. Its hammer circle is 40 inches in diameter. It is to be equipped with two fly wheels each weighing 2500 pounds, such that the total weight of the rotating system is approximately 7500 pounds. It will be mounted direct connected to the same 1200 speed, 100 h. p. motor. It will be fed with a 42-inch wide apron feeder capable of delivering up to 75 to 100 tons of feed per hour. This machine is equipped with screen bars to keep the large chunks in.

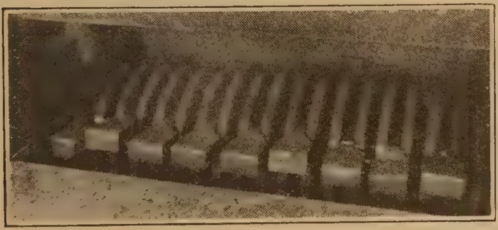

FIG. 9.

OGDEN ENGINEERING COMPANY,
OTTAWA, ILLINOIS

COMPARATIVE TESTS OF SOME AMERICAN AND GERMAN FIRECLAY BRICK[1]

By R. F. Geller and W. L. Pendergast

ABSTRACT

The Bureau of Standards has recently completed a short investigation comprising comparative tests of five brands of German-made brick and six brands of American-made brick. The results indicate that the German-made brick are practically the equal of the American brick.

Introduction

The fact that a specification for German naval high temperature duty clay brick has been recommended requiring a softening point not less than that of cone number 34,[2] while the United States Government Master Specification[3] requires a softening point not less than that of cone 31, made it seem desirable to determine whether or not the average qualities of the foreign-made brick were actually as superior as indicated.

Advantage was taken of the opportunity offered by the visit of Dr. Steger and Dr. Endell to this country in the spring of 1925 to arrange for coöperative testing of fireclay brick made in Germany and America, and for an exchange of the results obtained. It was believed that these results would also be of general interest to manufacturers and users of fireclay refractories and that the comparative data of two laboratories would be of particular interest to those engaged in the testing of clay products.

In a conference with Drs. Steger and Endell it was brought out that the difference in softening point requirements could be accounted for partly by differences in the cones used and partly by the German method of preparing the test cone. A chip is broken or sawn from the sample brick and ground down to the size and shape of the standard cone; consequently it has the relatively coarse structure of the brick and would not soften as readily as if ground to pass an 80-mesh screen, as is done in this country.

Scope

Specimens of five brands of brick, representing the product of eastern and western Germany, were obtained from abroad. In exchange, samples of seven brands were sent to Dr. Endell by three coöperating companies; these samples represented the product of the New Jersey, Pennsylvania, and Kentucky districts.

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[1] Published by permission of the Director, Bureau of Standards, Department of Commerce. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division.) Received March 1, 1926.

[2] *Tonind. Ztg.*, **44,** 1097–98 (1920).

[3] Bur. Stand., *Circ.*, No. 299.

District represented	Lab. no. of brand	Method of manuf.	Size, inches av. of 5 specimens	Weight		Chemical Composition SiO$_2$[a]	Al$_2$O$_3$[b]	Fe$_2$O$_3$[c]	TiO$_2$[d]
				lbs.	oz.	%	%	%	%
East. Germany	*A*	Stiff mud	9.7 x 4.7 x 2.5	8	5	54.9	39.8	2.0	1.9
	B	Hand made	9.8 x 4.8 x 2.5	7	15	60.6	33.9	2.2	1.3
	C	Hand made	9.6 x 4.5 x 2.6	7	7	59.3	34.5	2.0	2.0
West. Germany	*D*	Hand made	10.1 x 4.8 x 2.6	8	5	57.8	36.4	2.6	1.4
	E	Hand made	9.7 x 4.7 x 2.5	7	13	66.2	28.1	1.4	1.9
Av.				7	15	59.7	34.5	2.2	1.7
N. J.	*F*	Stiff mud	8.9 x 4.4 x 2.4	6	4	63.3	34.1	0.3	1.9
	G	Stiff mud	9.0 x 4.4 x 2.5	6	8	(75.8	20.5	1.4	2.1)[e]
Pa.	*H*	Dry press	8.8 x 4.4 x 2.4	7	1½	53.7	40.2	1.7	2.3
	I	Hand made	8.8 x 4.4 x 2.5	7	0	54.1	39.9	1.6	2.3
	J	Stiff mud	8.9 x 4.4 x 2.4	7	7	53.7	39.2	1.8	2.4
Ky.	*K*	Dry press	—	—		56.0	39.9	1.8	2.3
Av.				6	14	56.1	38.6	1.4	2.2

[a] Double dehydration
[b] (R$_2$O$_3$) Double precipitation
[c] Jones reductor
[d] Colorimetrically
[e] Not considered in average

TABLE II

Lab. no.	Load test[a] 1 specimen Deformation %	Endurance test Average 2 specimens[b] deflection in thirty secondths inch Deflection %	Remarks	Quenching test Average 5 specimens[b] Absorption after reheating %	Number of quenchings to produce failure	Softening point in cones	Absorption as received Av. 5 specimens %
A	2.3	14	Slight fracture	10.7	24	32	10.6
B	5.9	15		14.5	16	32	16.6
C	8.1	10		14.8	8	29–30	16.3
D	2.5	6		12.1	19	32	15.2
E	7.4	18	Bad fracture	11.0	15	31	13.5
Av.	5.2	13		12.6	16		14.4
F	3.6	6		16.8	34	32	18.3
G	0.0	13	Bad fracture	17.2	2[c]	30	15.5
H	1.8	11		8.9	29	32	8.0
I	4.6	12		10.0	17	32–33	10.9
J	4.8	6		7.9	9	33	9.2
K	1.0	—		—	33	33	—
Av.	2.6	10		12.2	21		12.4

[a] Standard A. S. T. M. test for heavy duty brick, C 16–20
[b] For details of method see Bur. Stand., *Tech. Paper*, No. 279

The foreign brick, and brick of six of the American brands sent abroad, were analyzed chemically; the softening points were determined and they were subjected to the standard load test for high temperature duty brick, the quenching test, and the endurance test.[1]

Results

The results obtained at the Bureau are given in Tables I and II.

With the exception of the brick made by the stiff-mud method, the foreign product is rather irregular in shape, but is strong, with sharp corners, and having a structure comparable with that of domestic manufacture. The size of the foreign product is consistently larger and the average weight is greater by one pound and one ounce.

Excepting the highly siliceous open-firing New Jersey brick, *G*, the German brick average 3.6% higher in silica, 4.1% lower in alumina, 0.8% higher in iron (as Fe_2O_3) and 0.5% lower in titania. In view of the general impression that German brick are siliceous, it was surprising to find the chemical compositions so nearly identical.

The group averages (Table II) show the German brick to be slightly less resistant to deformation under load in both the standard A.S.T.M. test and the endurance test, also less resistant to failure in the quenching test and approximately one cone lower in refractoriness. The differences in absorption are believed to be of no significance. In fact, the group results lead to the conclusion that the German brick are so slightly lower in quality that they can be considered as practically the equal of the American brick.

TABLE III

Lab. no. of brand	Temp. at which deformation began °C	Temp. at which specimen had decreased 4% in length °C	Softening point in cones	Alumina (Al_2O_3) content %
A	1250	1380	33–34	39
C	1270	1390	30–31	35
F	1150	1390		
G	1200	1460		
H	1260	1440		
I(*a*)	—	—		
J	1220	1400		
K	1150	1490		

(*a*) Not tested; apparently because brick was so friable that a specimen core could not be drilled out.

Comparison with Results of Tests Made in Germany

A progress report received from Dr. Endell, dated Dec. 11, contained no complete data other than results for the American brands and two German brands (*A* and *C*) obtained with a load test furnace described in a special leaflet of the Research Company for Refractories, Inc., Breite Strasse 3, Berlin-Steglitz. Since the tests were made on especially prepared specimens, under a load differing from that used in the A.S.T.M. Standard Test,[1] and the end point was taken as that temperature at which the specimen had decreased 4% in length, the results are not directly comparable. The data furnished by Dr. Endell are given in Table III.

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[1] For descriptions of these tests see the *Transactions of the A.S.T.M.*, and Bur. Stand., *Tech. Paper*, No. 279.

Summary

Group results obtained on brick of five brands made in Germany and brick of six brands made in this country indicate that the German brick are so slightly lower in quality that they can be considered as practically the equal of the American brick.

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[1] The load used was 2 kg. per sq. cm. A load of 25 lbs. per sq. in. is equivalent to 1.76 kg. per sq. cm.

THE ROLE OF SPECIFIC HEAT IN THE SELECTION OF REFRACTORIES[1]

By A. Ernest MacGee

ABSTRACT

A brief discussion of specific heats is given in which particular emphasis is placed upon its determination at high temperatures, the methods which have been used in the past for its determination, and the application of the values in the selection of refractories. The need of determining physical properties of brick which have been in service is pointed out.

History Joseph Black[2] was probably the first to illustrate the different capacities for heat of the same mass at different temperatures. It was in this connection that he originated the ice calorimeter which consists simply of two blocks of ice one of which is slightly hollowed out. In order to determine the specific heat of a substance by means of this apparatus, a weighed sample heated to the temperature in question is placed in the hollow of the one cake of ice and covered with the other. By noting the quantity of ice melted, it is a simple matter to calculate the number of calories of heat stored in the sample.

The work of Black was continued by Irvine[3] who was the first to publish a clear explanation disentangling the four entities, specific heat, mass, temperature change, and quantity of heat, when more than one was varied at a time. This work was conducted about 1770 and from then on the scientific world has had a clear conception of the phenomenon which enables different substances and the same substance at different temperatures to absorb different quantities of heat.

The work of Irvine was followed by that of Laplace and Lavoisier[4] who developed the ice calorimeter method to a fair degree of accuracy. Although Crawford[5] had probably been the first to use the method of mixtures, Dulong and Petit[6] developed it to a point where it could lay claim to scientific accuracy and made the first really reliable specific heat measurements. As a result of their determinations, they formulated their well known law.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division.)

[2] Lectures on the Elements of Chemistry, edited by J. Robinson, Philadelphia, 1807.

[3] Irvine, "Essays, Chiefly on Chemical Subjects," London, 1805.

[4] Laplace and Lavoisier, Memoirs de L'Academie de Science, 355 (1780). Ouevres de Lavoisier, **11**, 287, 725(1862).

[5] Crawford, "Experiments and Observations on Animal Heat." London, 1777–78; Philadelphia, 1787.

[6] Dulong and Petit, *Annales et de Physique*, **2** [7], **142**(1817). *Jour. Ecole Polytechnique*, **11**, 189 (1820). *Annales de Chemie et de Physique*, **2** [10], 395 (1819).

Definition By specific heat is meant "the quantity of heat necessary to cause a unit change of temperature in unit mass usually measured in C. G. S. units as calories per gram per degree centigrade." More simply stated: "Specific heat is the number of calories required from some external source to raise the temperature of one gram of material one degree centigrade."

Description Scarcely any two substances have exactly the same specific heat over any given temperature interval and the specific heat of most substances varies with the temperature. In the case of allotropic modifications of the same substance such as quartz and cristobalite, the form stable at the higher temperature generally has the greatest specific heat. Thus, cristobalite has a slightly higher specific heat than quartz. As a general statement, the specific heat of a substance decreases with the temperature, that is, more heat is required to heat a given substance (fire brick) from 100 to 101°C than from 900 to 901°C. However, the value ordinarily desired is not the specific heat at any particular temperature but the interval specific heat; that is, the average specific heat over a given temperature range of, say, 25 to 1200°C. Interval specific heat increases with increase of temperature; *i.e.*, the specific heat over the interval 25 to 500°C will ordinarily be less than over the interval 25 to 1000°C.

The specific heat of some substances may vary quite perceptibly over any given temperature range owing to the fact that thermal changes are taking place. If an endothermal process is taking place such as the conversion of alpha to beta quartz or the driving off of chemically bound water, the specific heat will be abnormally high. This is quite apparent when one recalls that in order to raise the material to the temperature in question, sufficient heat must be added not only to heat the material as such but, also, to supply heat for the heat absorbing process. On the other hand if an exothermal process is taking place such as the oxidation of sulphur or the thermal processes which clays undergo at about 950°C, the specific heat will be abnormally low. The specific heat over any given interval will, of course, depend upon the net result of all endothermal and exothermal processes which the material may undergo. In the case of many ceramic materials, such as the clays for example, these thermal processes are very intense and, by all means, must be taken into consideration in determining their specific heats. Ordinarily, fired materials undergo only slight thermal processes which can be disregarded in specific heat determinations.

Methods The determination of the interval specific heats of many ceramic materials is greatly complicated owing to the fact that they often undergo thermal processes on heating which are not reversed on cooling, such as the decomposition of carbonates, firing of combustible matter, etc. That is, they do not evolve the same amount of heat on cooling as they absorb on heating. The procedures which have been employed in the past to determine the specific heat of a given material can be classified under one or more of the following general methods:

1. From calculations based upon the law of Dulong and Petit and which require no experimental determinations. This law states that the product of the specific heat and the atomic weight of the solid elements is constant, being approximately 6.4. However, it is not applicable to ceramic materials as the specific heat of the various materials changes with temperature sufficiently to invalidate it.

2. From data obtained by a method based on Newton's law of cooling, which states that the time taken by equal masses of substances under exactly identical conditions in cooling through equal ranges of temperature is directly proportional to their specific heats. This method is, at best, inaccurate and is not to be recommended.

3. From data obtained by measuring the electrical energy required to heat the sample to a given temperature—the current passing through the test piece. This method is, unfortunately, limited to conductors of the first class and is thereby inapplicable for measuring specific heats of ceramic materials.

4. From data obtained by measuring the electrical energy required to bring the material, contained in a calorimeter, to a given temperature. Navias, at the University of Illinois, used a modification of this method and gave to the scientific world for the first time accurate figures for the interval specific heats of materials which undergo irreversible thermal changes. The calorimetric methods give very accurate values but are expensive to construct and are, usually, quite complicated in their operation.

5. From data on heat required to bring the material to a given temperature as calculated from curves obtained by a differential thermal method. This method was worked out by Cohn in Germany and gives values which take into account all thermal changes. The method is rather simple and the apparatus relatively inexpensive but the values it gives are not as accurate as those obtained by the calorimetric methods.

6. From data obtained in a differential thermal method in which the temperatures attained by the sample and a reference substance are measured after a definite heat treatment. This method was worked out by MacGee at Ohio State University and gives values which include all thermal processes the material may undergo. However, the results are not as accurate as those obtained in the calorimetric methods. It should be pointed out here that these methods which account for all

thermal processes, irreversible as well as reversible, have given values for the interval specific heats of raw clay and green bodies which are fully one-third higher than the values formally accepted. Obviously, this means that our ceramic kilns have been and are operating at a considerably higher efficiency than has ordinarily been supposed.

7. From data obtained by the procedure known as the method of mixtures. This involves heating the weighed unknown to the temperature in question and allowing it to fall into a calorimeter. Thus the quantity of heat it contains at the time of dropping can be measured and its specific heat calculated. In this method (as well as in that based on Newton's law of cooling), it is assumed that the heat evolved on cooling is equal to that absorbed on heating. Therefore, this method is inapplicable for specific heat measurements where the material undergoes irreversible thermal changes. Fortunately, fired materials such as chrome brick, fire brick, etc., undergo no appreciable thermal changes on heating and most of the thermal changes which silica brick undergo on heating are reversed on cooling so that this method is applicable for determining specific heats for refractories. Owing to its relative accuracy, ease of manipulation, and relative inexpensiveness, this method is to be recommended for the determination of specific heats of fired refractories over the entire temperature range in question.

Part Played by Specific Heat

The part that specific heat plays, or should play, in the selection of refractories is of decidedly more importance than the average technical man considers. This is true because, until thermal equilibrium has been reached, the influence of heat conducted across the brick in causing a temperature rise is not determined by the conductivity solely, but by the heat capacity per unit volume of material—the greater the latter the smaller the temperature rise produced by a given quantity of heat. In all heating and cooling operations, it is the thermal diffusivity and not the thermal conductance with which one is principally concerned.

The thermal diffusivity, $d = K/c \cdot s$ in which, c = specific heat, s = specific gravity, K = thermal conductivity, and d = rise in temperature produced in one cubic centimeter of the substance by one calory flowing in one second through one square centimeter of a layer one centimeter thick, having a temperature difference of one degree centigrade between its faces.

Thus one sees that specific heat and specific gravity, as well as thermal conductivity, are of vital importance when one is considering the relative ease with which a given refractory can be heated or cooled.

For instance, assume equal thermal conductivities: The greater the specific heat and specific gravity of a brick the greater will be the quantity of heat that can be stored but the longer it will take to heat it to any given temperature. On the other hand, the less the specific heat and specific gravity of the brick the less will be the quantity of heat that can be stored but the quicker it can be heated to any given temperature.

The following table shows the values obtained by Tadokoro[1] for various types of brick.

THERMAL DIFFUSIVITY OF VARIOUS BRICKS

Temperature	Magnesia	Chrome	Silica	Common red	Fire clay
200°C	6.57	5.55	4.90	2.25	2.80
300	5.47	5.71	5.25	2.08	2.95
400	4.91	5.99	5.68	1.94	3.59
500	4.71	6.01	5.41	1.85	3.96
600	4.39	5.79	5.35	1.56	3.69
700	4.14	5.45	5.29	1.44	3.39
800	3.85	5.10	5.48	1.32	3.69
900	3.73	4.77	5.41	1.23	4.02

The diffusivity of magnesia and common red bricks decreases with rise in temperature. For silica, fireclay, and chrome bricks, the diffusivity increases with the temperature. Hence, it is to be concluded that silica brick are most suited for installation of a reservoir of heat, the temperature of which is required to rise as quickly as possible when hot gases come into contact with them, and to cool quickly when cold gases come into contact with them. Also, it is to be concluded that fireclay brick are better heat insulators than silica brick. The conclusions drawn from these data are in harmony with the experiences of practical men in the plants.

Since the thermal diffusivity is greater the less the specific gravity, one might suppose that high porosity would be desired in a brick. In this connection, J. W. Mellor[2] has suggested that the heat insulating properties of pores will vanish at high temperatures. This is on account of the increase in importance of the radiation of heat across the pores with rise of temperature as compared with the conduction of heat through the solid material. The transmission of heat by radiation across a pore is, according to Stephan's law, proportional to the difference in the fourth power of the temperatures, whereas the conductivity in the solid material depends on simple temperature differences. However, it can be shown that the transmission of heat by radiation across the pores only becomes as great as that by conduction across the solid material at a temperature of about 3600°C. So that only at temperatures far above the melting points of refractories does the heat insulating effect of the pores vanish.

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[1] Tadokoro, "On the Determination of the Thermal Conductivity, etc.," *The Science Reports of the Tohoku Imperial University*; 1st series, 10 (1921).

[2] J. W. Mellor, *Jour. Gas Lighting*, March 10, 1914.

In conclusion, I would say that there are very accurate values in the literature for the specific heats of practically all of the common refractories over the entire range, 20 to 1400°C. Although an adiabatic method is more or less impractical, it is doubtless, from a theoretical standpoint, the most desirable of all methods for ceramic materials. In order to determine interval specific heats by this method, one would heat an outer furnace without heat flow to or from an inner furnace containing the sample and measure the electrical energy required to bring the system to any temperature. If further interval specific heat values are desired for fired refractories, I would suggest the use of one of the modifications of the method of mixtures for determining the values over the entire temperature range, 20 to 1400°C.

I feel that it would be quite desirable to have an investigation conducted with the object of determining specific heat, specific gravity, and thermal conductivity on brick which have been actually in service for a considerable period of time. This is because the character of the brick changes with use.

Lord Hall, O. S. U.
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RECENT FACTORY EXPERIENCE AND EXPERIMENTS IN DRYING TERRA COTTA[1]

By James R. Bowman

ABSTRACT

An attempt was made to determine by experiment the best conditions with respect to temperature, circulation of air, and its relative humidity, by which to obtain shorter drying time, a minimum of warpage, and cracking of the ware generally. Also, a very tender clay was given special study with the object of finding a set of drying conditions by which its extreme tendency to warp and crack would be reduced to a point that would permit practical use of this clay for terra cotta body. The drying time was reduced about 40% by increasing the steam pressure in the heating coils and apparently some showing made in reducing the tendency of the ware to warp and crack. A schedule of drying that gave satisfactory results with the tender clay was developed on an experimental scale, but could not be applied to the factory driers because of limitations in the heating and circulation equipment.

Introduction

During the past year the Midland Terra Cotta Company has been confronted with two problems in connection with the drying of terra cotta: (1) To increase the output of its three Carrier driers and at the same time minimize the warpage and cracking of the ware. (2) To determine whether it would be practicable to use, in regular practice, a certain clay which was available but which showed a strong tendency to warp and crack in drying.

Drier Practice at Time Work Was Started

The three driers which are identical in dimensions and equipment are 28 feet long, 13 feet wide and 10 feet high, inside dimensions. They are equipped with 6 sections of heating coils, each section having 56.5 square feet of radiating surface; automatic control valves for controlling admission of steam to the heating coils; and a steam spray device for raising the relative humidity, when desired. This steam spray was automatically controlled by a hygrostat. The fan for furnishing circulation of air is a Niagara duplex connoidal type, size 3½, which is driven at 1085 r.p.m. and delivers about 4,000 cubic feet of air per minute under pressure of one inch.

As is probably the case with all Carrier driers of this type, the duct from the fan to drying chamber terminates in a header fitted with ejector nozzles so shaped and placed that the hot air emerging under a pressure of approximately one inch, has a sort of jet action and picks up other air, inducing a circulation within the drying chamber which is said to be several times as effective as it would be without the ejector action. It should be stated in this connection that these are the first or among the first of the driers equipped by the Carrier Company for drying terra cotta and that they have since found by experience that better results can be obtained by arranging the ejector nozzles at the side, thus causing the direction of circulation to be crosswise the chamber, instead of lengthwise as is the case with our driers which have their ejector nozzles at the end. This should be taken into consideration in connection with the results obtained.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Terra Cotta Division).

The housing of the heating system has an opening at its end opposite that where the fan is located for admission of fresh air when drying, and also two hinged doors at its side for additional fresh air for rapid cooling of the chamber of ware after drying has been completed. An opening to a chimney in the wall of the drier provides a means for the escape of moist air from the drying chamber.

The arrangement of the ducts and ejector nozzles is shown briefly in Fig. 1.

Operation, Early Practice The usual practice was and is to load each of these chambers with from 14 to 17 tons of terra cotta, on pallets supported on legs.

It was customary to start a chamber with 10 pounds of steam on four of the sections of coils and with the fresh air damper open. The hygrostatically controlled steam spray was set for 65% relative humidity and actually held the humidity between 60 and 70% up to the time at which the dry bulb temperature in the chamber reached 125°F. At this point the spray was automatically shut off and 50 pounds of steam automatically turned into the remaining 2 sections of coils. The time required to reach this temperature was from 3 to 4 hours. This arrangement was left unchanged until the end of the drying period, which was 38 to 42 hours total drying time.

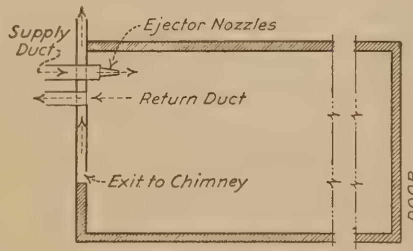

FIG. 1.—Showing arrangement of the supply duct, the ejector nozzles, the return duct, and the outlet to the chimney for escape of moist air, in the Carrier driers.

Under the above conditions the temperature inside the drying chamber rose at a fairly constant rate from that of ordinary room atmosphere to about 140°F in 8 hours. From then on the rate of rise was much slower, reaching a maximum of 165 to 170° at the finish.

The relative humidity started to drop immediately after the spray was stopped and went gradually from the maximum of about 65% to a minimum of 12 to 15% at the finish.

With this method of operation the drying time of the ware was, as stated above, from 38 to 42 hours. Some warping of the ware occurred and usually about 2% of it cracked. In some cases the cracks were large and deep, and in others they were small, shallow, surface cracks, which seemed to be caused by condensation of water on the surface during the drying process.

Experiments Made with the Carrier Driers

A number of experiments were made with the driers, in each of which the original method of operation, as described above, was varied in some particular; the object was to find some set of conditions which would make possible a shorter drying time and also reduce the tendency of the ware to warp and crack.

Most of the experiments made were repeated a sufficient number of times to make the results definitely conclusive.

In each of these experiments the loss of weight of one piece of ware was determined by means of an ordinary platform scale located above the drying chamber. The test piece was suspended from the scale by a wire extending through a hole in the top of the chamber. A piece weighing about 75 pounds was selected for this purpose in each case.

A record of the temperature change in one piece of ware was obtained by means of a recording psychrometer, with its wet bulb buried in the piece. A wet and dry bulb thermometer set was used for determining relative humidities.

Relative Humidity Increased One set of experiments was based on the assumption, that by carrying a high relative humidity in the early stages, a relatively high temperature of ware would be attained and that this would result in shortening the subsequent drying period as well as reducing warpage and cracking.

Relative Humidity Decreased Another set was tried to determine the effect of carrying a lower relative humidity in the initial stage, so as to accomplish a reasonable amount of drying during this period, thereby leaving less work to be done after the stopping of the spray. One of the considerations in this case was the avoidance of fine cracks resulting from condensation on the ware.

Circulation Increased In order to obtain more rapid circulation of air in the drying chamber, the fan speed was increased from 1085 to 1200 r.p.m.

Regulation of Fresh Air Inlet An attempt to bring up the temperature rapidly was made by keeping the fresh air inlet closed during the steam spray period, then keeping it half open for 14 hours and finishing with it completely open.

Results of above Experiments None of the changes numerated above affected the final results to any important extent. The records obtained all seemed to point to the conclusion that what was needed was more heating capacity.

Use of Increased Steam Pressure On the strength of the information obtained in the previous experiments, it was decided to use boiler pressure, 90 to 100 pounds, on the two high pressure sections of coils instead of 50 pounds. This caused a decided reduction in the time required to dry the ware, bringing it down from about 40 to about 34 hours which was a saving in time of about 15%. No change in the tendency of the ware to warp and crack could be detected.

This change had been tried out, initially, on only one of the three driers. The improvement seemed to justify making the same change on the other two and this was accordingly done.

Experiments with a Small Drier

Our experiments with the full size driers were subject to certain limitations. First of all some consideration had to be given to the question of safety to the ware in the drier; but the most serious limitations were in the heating capacity and the air circulation. It was thought that better progress could be made and with less expense by doing a certain amount of experimental work on a small scale, with a drier in which we could raise temperatures as rapidly and as high as desired and in which a more vigorous circulation could be obtained.

An experimental drier was accordingly built for the purpose. The drying chamber was made of one-inch lumber, having inside dimensions 32 inches wide, 36 inches high and 48 inches long and lined with galvanized sheet iron. Its top was made removable to permit loading and unloading of the ware. The steam heating coils were arranged inside, at the bottom of the drying chamber, as was also a steam spray device. A small fan with electric motor attached was arranged at one end of the drier, near its top, and made connection with the drying chamber by a supply duct near the top of the chamber and a return duct near its bottom. The return duct contained a small vent for admission of fresh air to the system.

The drying chamber was equipped with a scale for measuring the loss in weight of a piece of ware; a psychrometer, which was used for measuring the temperature of the interior of a piece and a dry and wet bulb thermometer set for measuring relative humidity.

The drier with its equipment is illustrated briefly by Fig. 2.

The clay from which the ware was made for use in the tests was a coal measure clay, from Greene County, Southwestern, Ill. This clay which is available and offers a source of additional supply seemed to be suitable for terra cotta, with the exception of its strong tendency to warp and crack, which had resisted all attempts to dry safely in the Carrier driers.

It should be stated that during the time that the experiments on this tender clay were being conducted in the drier a slow drying test was also made, using the same kind of pieces as those used in the drier. This was done by putting several pieces on pallets on the floor of a room whose temperature was about 100°F and which contained no forced circulation of air and leaving them there until they were dry, which required 3 to 4 days' time. Under this treatment the amount of warpage was small and only one piece cracked.

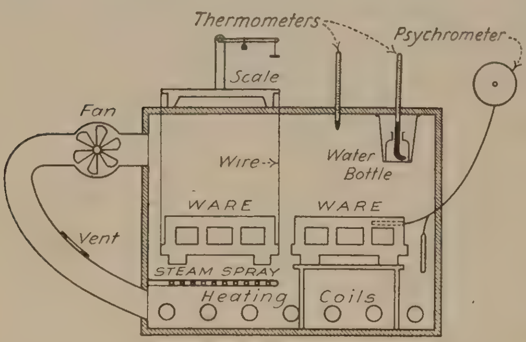

FIG. 2.—Showing arrangement of the equipment, the test apparatus, and the position of the ware, in the experimental drier.

It was assumed that if any set of conditions was found whereby this particular clay could be dried safely at a rate which would be practicable they would give equally as good results with most of the clays used in the manufacture of terra cotta.

In the experiments two pieces of ware were dried at each test. They were rather large base pieces, having dimensions $4\frac{3}{4}$ x 17 x 18 inches, a form of piece which tends to give trouble by cracking when dried in the plant driers. They were taken immediately after they were dumped from the molds, finished, and the drying process started at once. Ordinarily this treatment would be considered severe, as in our usual practice it has been found essential to allow the ware to stiffen up somewhat before loading it into a drier.

The writer had found by previous experiments that the dry shrinkage of a piece of ware is complete when it has lost about 60% of its free water, which in our case is about 11% of the wet weight of the piece. This was found to be true of the clay used in these drying experiments and also of two other clays. The conclusion was made therefore, that during the time shrinkage is taking place the rate of drying should be controlled within certain limits, so as to make possible a more uniform rate of shrinkage throughout the piece, but when the shrinkage period in the drying has been completed, the danger of warping and cracking is passed and drying may be hastened from that point on to completion without injury to the ware.

The rate of drying during the shrinkage period was varied for different runs, in order to find the rate which was best suited to the safety of the ware. This was done by varying the relative humidity by means of the steam spray and noting the loss of weight every half hour, of a piece which was suspended by wires fastened to the scale on top of the drier. A record was also kept of the vapor tension, vapor pressure difference, which is a criterion of the rate of evaporation. In each case when the ware had lost 11 to 12% in weight, (which required about 7 hours' time) the steam spray was stopped and the drying let take its course from then on to the finish.

It was thought that with complete recirculation, that is, with no opening for the admission of air to the system, evaporation from the test pieces would keep the humidity sufficiently high for good results, even with rapidly rising temperature. The first run was accordingly made without the use of a steam spray. The humidity did not go up as anticipated and the ware cracked badly. This may have been due, to some extent, to leakage of air into the apparatus but it seems probable that evaporation simply did not take place rapidly enough to compensate for the rapidly rising temperature.

Thereafter, the steam spray was used in increasing amounts, thereby raising the relative humidity and making a gradual improvement in the ware with respect to cracking, until a set of conditions was reached under which the ware could be dried with very little trouble from cracking. Cracking could not be eliminated altogether, however, until provision was made for admission of better circulation at the bottom part of the piece where it was protected to some extent by the drying pallet. This was done by perforating the pallet with holes and arranging a pipe to deliver a strong current of air under the pieces. With this equipment the ware could be dried free from cracks.

The best results were finally obtained as follows: after the ware was arranged in the drier and the equipment put in order the fan was started and run at room temperature for 2 to 3 hours by which time the ware had lost about 1% of its weight. Steam was then admitted to the heating coils and the dry bulb temperature in the drying chamber rose quite rapidly from that of the room to about 195°F in 4 hours. From then on until the ware was dry, which was from 12 to 14 hours total time, it rose constantly up to 210 to 215°F.

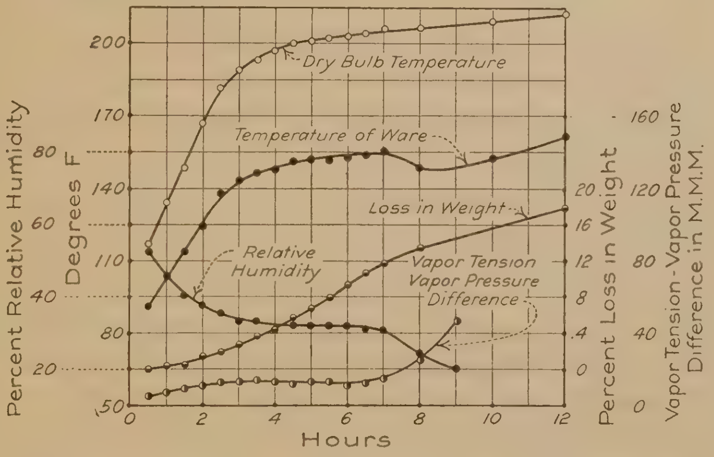

FIG. 3.—Conditions of temperature are shown, relative humidity, rate of drying, etc., with the experimental drier. This set of conditions gave satisfactory results with respect to the safety of ware which was made from a very tender clay.

By this procedure it was found possible to dry the test pieces in the time stated without cracking and with an amount of warpage considerably less than that which occurred with duplicate pieces dried in the plant driers. It should be stated, however, that the warpage was somewhat more than that which took place in similar pieces dried more slowly, on the regular factory pallets in a warm room.

Figure 3 shows the factors of temperature, loss in weight, relative humidity and vapor tension, vapor pressure difference, all plotted against time in hours. The set of conditions represented here in graphic form gave the most satisfactory results. It was quite definitely concluded, that the conditions for drying which were worked out with the experimental drier to give good results, would also give equally as good results on a plant scale. It was realized however, that the problem would be more difficult on a larger scale, because to get the proper circulation of air over all surfaces of the ware would be harder to accomplish in the case of a large quantity of it stacked together than it was in the case of two pieces in the small drier.

The decision was made, at any rate, to duplicate as nearly as possible in the Carrier driers, with their present equipment, the conditions of temperature and relative humidity by carrying steam pressure of 90 to 100 pounds in all of the 6 sections of heating coils during the total time of drying and by using the steam spray for a longer time in the initial stages than had been practiced previously.

Attempts to Duplicate Results of Experimental Drier in the Plant Driers

The clay used for making the ware which was dried when making these experiments was largely that in general use in our plant at that time. It was a coal measure clay from the Brazil district of southwestern Indiana. Its tendency to warp and crack in drying was probably not above the average of that of the various clays in common use in the manufacture of terra cotta. Also a few pieces made of the same tender clay that was used in the small drier were dried each time.

The ware was allowed to remain on the floor of the pressing shop for the usual length of time before loading it into the drier, after which the drier was loaded the usual way, except for the weight of ware which was smaller, being from 7 to 9 tons for each run. That quantity was not sufficient to fill the drier, so a wider space than usual was left at the front part of the drier and the required space of about 30 inches overhead and at the rear.

The pieces made of the tender clay and by the same mold as those used in the small drier, were placed, some of them near the front part of the stack of ware and some near the rear part. One piece was suspended from the scale for measuring the loss of weight, also the psychrometer tube was imbeded in one of them for measuring its interior temperature rise.

The fan and steam spray were started working and boiler steam pressure of 90 to 100 pounds admitted immediately to all of the 6 sections of heating coils.

The relative humidity was kept regulated by means of the steam spray so as to allow practically no evaporation of water from the ware, as indicated by the scale during the first 3 to 4 hours. In fact the scale showed in most cases a gain in weight during the first hour or so, as may be seen by the "loss in weight curve," Fig. 4.

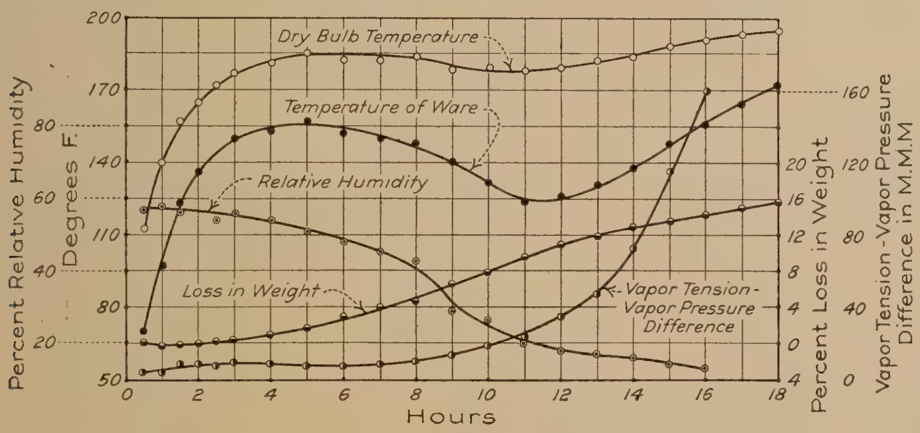

FIG. 4.—Showing conditions of temperature, relative humidity, rate of drying, etc., with the Carrier drier, when trying to duplicate there the results of the experimental drier. This set of conditions was not a duplicate of that obtained with the experimental drier, neither were the results satisfactory.

The object in checking drying during the first part of the run was to allow the temperature of the ware to go as high as possible, on the assumption that if the ware is at a relatively high temperature, drying may be allowed to proceed more rapidly and will at the same time be safer, because of a more rapid diffusion of water to the surface, thus maintaining a more uniform rate of shrinkage.

At the end of this 3 to 4 hours' heating-up period the relative humidity was made to drop somewhat more rapidly by reducing the steam spray and the drying thereby increased. This likewise caused a drop in the temperature of the ware.

After 3 to 4 hours' additional time the steam spray was stopped altogether and the drying allowed to take its own course from then on to the finish, which was about 18 hours' total time. This stopping of the spray caused a considerable drop in the relative humidity, a rapid increase in the vapor tension, vapor pressure difference and also a further lowering of the temperature of the ware, all of which are indicative of a state of relatively rapid drying. Rapid drying at this time was further confirmed by an increase in the percentage loss in weight as indicated by the scale. The conditions of temperature, relative humidity, loss in weight, etc., may be seen in more detail in Fig. 4.

When these experiments were in progress a number of runs were made in which the above schedule was followed for the most part. A few variations in the fresh air supply were made, however, by closing or partly closing the fresh air vent during the first stages of the drying, none of which seemed to materially affect the results.

By using 7 to 9 tons of ware the drying time was reduced to about 18 hours. This reduction of the time necessary to dry the ware was partly due to the use of a smaller quantity and partly to an increase in temperature, caused by using steam of higher pressure on all of the heating coils for the total time of the run.

The condition of the ware with respect to warpage and cracking was not so good as it was in the case of the former method of slower drying at lower temperature. Practically all of the pieces which were made of the tender clay cracked, with the exception always of the piece which was suspended from the scale in each run. The ware which was made of the clay in regular use at the plant, which constituted most of that which was dried in the experiments showed a stronger tendency to crack also, but the cracks were small and shallow and seemed to be due to condensation of water vapor on the surface of the ware.

After studying the results of these experiments it was concluded that the results obtained in the small drier could not be duplicated in the regular plant driers for the reason that the temperature and circulation conditions could not be duplicated. The dry bulb temperature inside the drier was not nearly so high and to obtain as nearly uniform circulation of air over all exposed parts of the ware in case of a large quantity of it stacked together, was impossible with the present equipment and system of setting.

The primary cause of cracking in this case, seemed to be the lack of the proper circulation of air. A secondary cause was that of insufficient heating capacity to keep the temperature of the ware sufficiently high during the shrinkage period of the drying.

Further Experiments with the Carrier Driers and the Present Method of Operation

Having failed in the attempt to duplicate the conditions and results of the small drier in the Carrier driers the original method of operating the Carrier driers was resorted to, somewhat in detail, with the exception of the steam pressure in the heating coils. In this case the steam pressure was 90 to 100 pounds, which as stated previously, was higher than that originally used.

The original practice of loading the driers to full capacity (14 to 17 tons), admitting steam to only part of the heating coils and at the same time using the steam spray for the first 3 to 4 hours of the run, then stopping the steam spray and turning steam into the rest of the heating coils for the rest of the run was given a trial.

The results seemed to show that this was the best method by which to operate. The time required to dry the ware in this way was found to be about 24 hours and the tendency to warp and crack was much less than it was in the case of the admission of high pressure steam to all of the coils at the beginning and seemed to be even less than that when using steam of lower pressure throughout the entire run, in which case the drying time was much longer.

Having obtained favorable results by the use of high pressure steam on all of the heating coils of one drier, the other two which were still running with steam of low pressure in part of their coils, were changed to high pressure also. Quite satisfactory results were obtained in this way with all three driers. For 18 runs in which a check was kept on conditions and results, the average drying time was 24 hours and the amount of ware cracked was .32% of that dried.

Obviously, these results were a decided improvement on those obtained in which the drying time was about 40 hours and the quantity of ware cracked about 2% of that dried.

While the above scheme of operating the driers gave very satisfactory results, as compared with the former practice, it was obvious that if the use of the steam spray in the initial stages of the drying could be eliminated, without injury to the ware, the method of operation would thereby be simplified. So drying without the use of the steam spray was given a trial and proved to be as satisfactory as with its use. Therefore, the three driers have been operated since without the use of the steam spray.

Briefly, the present procedure in drying is to load a drier to near its capacity (14 to 17 tons) with ware that has remained on the floor of the pressing shop for 24 hours after it was pressed. Steam is admitted to 2 sections of the heating coils, the fan started and the fresh air vent left open. After 3 to 4 hours' time, steam is admitted to the remaining 4 sections of heating coils and the side door next to the fan, in the housing of the heating coils, opened. Opening this door permits a certain amount of unheated, fresh air to be drawn into the drying chamber thereby preventing a sudden, rapid rise of temperature when steam is turned into the last 4 sections of heating coils. After 3 to 4 hours' additional time the side door is closed and the drying finished without any further attention. Figure 5 shows the conditions in the drier during the drying process.

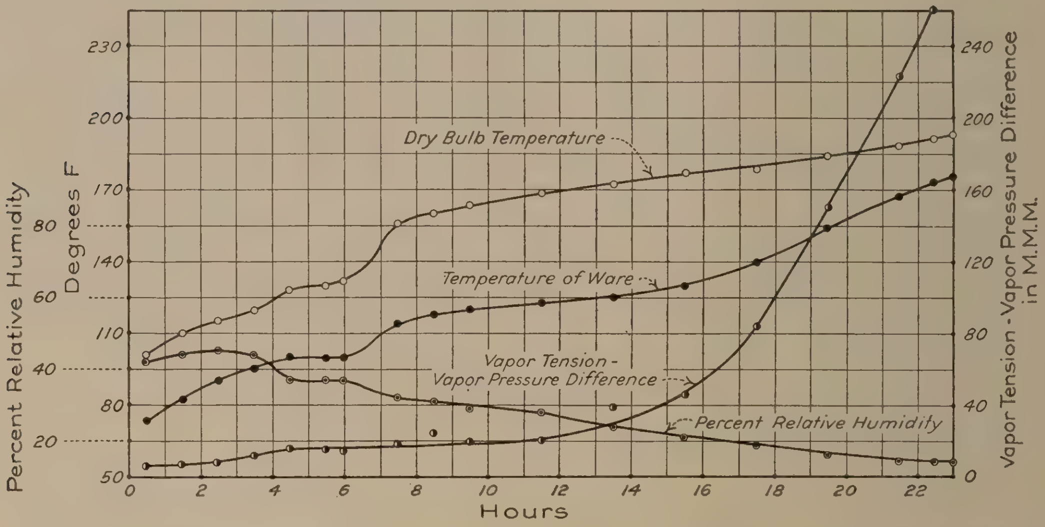

FIG. 5.—Showing conditions of temperature, relative humidity, etc., with the present method of operating the Carrier driers in which no steam spray is used. These conditions give good results.

Although this scheme works well with the clay which is in use at the plant at the present time, it is conceded that it probably would not be satisfactory with more tender clays.

General Conclusions

It seems quite evident from the results of the above experiments and from experience in general that terra cotta may be dried very rapidly and at the same time have its tendency to warp and crack minimized, if the conditions of temperature, relative humidity, and the circulation of air are properly controlled.

For rapid drying the heating capacity is of primary importance. Other conditions remaining constant, the rate of evaporation increases with rise of temperature and will proceed no faster than the rate of heat transfer from the heating medium to the ware. Therefore, if rapid drying is to be carried on, the heating capacity should be sufficient to maintain a relatively high temperature of the circulating air. This is very important if drying is to proceed rapidly while shrinkage is taking place, because of the more rapid diffusion of water from the interior of the ware to the surface with elevation in temperature. Those parts of the ware which are better exposed to the circulation of air, dry fastest and consequently shrink more rapidly than the parts which are less exposed, thereby creating a condition favorable to the tendency to warp and crack and any condition which hastens the migration of water to those most rapidly drying parts of the surface; thus maintaining more uniformity in the distribution of water throughout the piece, is an aid to a more uniform rate of shrinkage.

Relative humidity is a controlling factor for the rate of evaporation and also for maintaining higher temperature of the ware. An increase in the relative humidity of the circulating air means an increase of the temperature of the ware, because of its slowing down evaporation which is a cooling action. Even with ware of relatively high temperature there is an upper limit to the rate at which drying can proceed safely during the shrinkage period. Therefore it is important to carry such relative humidity as will limit the drying to that rate.

A very important factor concerned with uniform and the consequent safe drying of the ware is that of the circulation of air. This is especially true when drying rapidly at high temperature. The impossibility of obtaining uniform circulation over all exposed surfaces of the ware in case of a relatively large quantity stacked comparatively close together in an enclosure is important. Were it possible to obtain uniform circulation over all exposed surfaces, including those of the webs and the interior, the rate of shrinkage throughout the piece would most likely be uniform. This much desired condition is impossible to obtain in practice however, and the only recourse is to approximate it as closely as possible.

Drying a very tender clay safely, at a rapid rate, in the small drier and not in the plant drier was due primarily to our being able to obtain more uniform circulation over all surfaces of the ware in the small drier. In the larger drier the temperature of the ware was not kept high enough. To keep the temperature of the ware sufficiently high in the larger drier it was necessary to carry higher humidity and this resulted in condensation which caused small surface cracks.

In plant practice we have found a very valuable aid to safe drying to be that of allowing the ware sufficient time to stiffen up somewhat before application of heat. This may be done by leaving it on the floor of the shop for a time after pressing before it is loaded or by circulating air of room temperature in the drier for a few hours before applying heat in the drying process. We practice the former method. It has been found that omission of this practice results in an increased tendency of the ware to warp and crack.

Midland Terra Cotta Co.
Cicero, Illinois

NOTES ON GREEN SCUMMING[1]

By Earl R. Curry

ABSTRACT

A description of a green scum formed on brick made from a California clay. Analysis showed vanadium oxide as the principal colorant. Tests of scum prevention were made by adding various compounds to the green body or by dipping the finished piece into solutions of various salts. Several promising methods of scum prevention are indicated.

Introduction

By green scumming we refer to a greenish yellow to green efflorescence appearing on the surface of a fired fireclay body after moisture has been absorbed and evaporated from the ware.

Causes of Green Scumming Two explanations of this phenomena have been advanced: (1) It is sometimes said to be due to a growth of low organisms, an algae; or (2) it may be caused by colored soluble metallic salts in the body.

Seger[2] found in one case that the scum was caused by a chromium compound, and in another that the salt contained vanadium and molybdenum compounds.

C. W. Hill[3] has attributed the stain to ferrous salts.

Source of Clays The clays referred to in these notes are from the Sacramento Valley, California. They are mined near Lincoln and near Ione. The efflorescence-forming minerals seem widely and more or less uniformly distributed.

How the Scumming Develops

The terra cotta and light shades of brick on which the phenomena appears are fired to cone 4. After the fired ware has been set out in the open and has had the opportunity to absorb water and to dry, the scumming shows on the face from which the drying takes place. It is usually a greenish tinted yellow color later changing to a deep green color, although both colors *sometimes* appear side by side. An oxidizing agent such as hydrogen peroxide changes the green salt to a yellow color. Some of the ware, after periods of prolonged soaking and drying, will develop a heavy coating of scum which is readily soluble in hot water.

Analysis

Brick which had weathered a considerable period of time, and on which a heavy coating of green scum had appeared, were taken and the easily soluble salt dissolved in hot distilled water. A sample was carefully prepared by concentrating this solution and filtering through ordinary laboratory filter paper. The solution was green and on evaporation to dryness yielded a green salt.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Terra Cotta Division.)

[2] Herman A. Seger, Collected Writings, **1**, pp. 381, 386.

[3] *Bull. Amer. Ceram. Soc.*, **1**, 51(1922).

This sample was submitted to Smith Emery and Co., a commercial chemical laboratory of San Francisco, for qualitative analysis. Their report was as below:

Examination of green scum shows as follows, quantitative figures being given when complete separation was necessary to a careful analysis:

	Per cent		Per cent
Silica	Small amount	Cobalt oxide	Nil
Alumina	Small amount	Vanadium oxide (V_2O_5)	7.71
Iron oxide (Fe_2O_3)	0.15	Manganese	Trace
Arsenic	Nil	Magnesia	4.27
Copper	Nil	Potash (K_2O)	4.60
Lead	Nil	Soda (Na_2O)	5.01
Molybdic oxide (MoO_3)	1.65	Sulphuric anhydride (SO_3)	17.60
Nickel oxide	1.00		

Note: About one-half of sample is water of crystallization and organic matter, containing much nitrogen.

Interpretation of Analysis

This analysis indicates a mixture of several salts. Evidently there may be metavanadic acid, and sulphates of vanadium, nickel, and iron. Possibly vanadium molybdate or molybdenum vanadate may be present. Sodium and potassium vanadate may be a part of the mixture. There probably are vanadates and sulphates of sodium and potassium. It seems certain, however, from the analysis, that vanadium is the main element contributing to the discoloration.

Vanadium being one of the rarer elements the properties of but few of its compounds are definitely known. This fact makes the search for scum counteracting agents that much more difficult. As an example of the valencies with which vanadium may combine with other elements, its sodium compounds are here included.[1]

Sodium metavanadate	$NaVO_3$	Sodium tetravanadate	$Na_3HV_6O_{17}$
Sodium orthovanadate	Na_3VO_4	Sodium hexavanadate	$Na_2H_2V_6O_{17}$
Sodium pyrovanadate	$Na_4V_2O_7$		

The presence of nickel is *noteworthy* as thus being one of the scum-forming elements.

The presence of organic matter indicates an organic growth or algae. Probably the constitution of the soluble salt provides a favorable condition for this organic growth to develop.

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[1] Thorpe, Dictionary of Applied Chemistry, **5**, p. 611, Longmans, Green and Co., New York.

Study of Methods for Preventing Green Scumming

There are two apparent methods of preventing the appearance of the efflorescence: (1) by adding some counteracting salt to the raw body, analogous to the well known use of barium carbonate, (2) by dipping the fired ware in some counteracting solution, where this is possible or economical.

1. Adding Salt

Use of Lead Discussing the first method, it appears that there are salts which at least hinder the development of greening. However, the discovery was made (it has been known for some time among some at least) that the use of a lead salt when added to a raw body hinders the development of scumming on the finished ware. Basic lead carbonate or white lead, being easily and more or less cheaply obtained, naturally comes to mind as the salt to use. Experiments have been run, in a laboratory way, to determine just how effectively lead serves as a preventative.

In making these tests, a terra cotta body was used. This body has an absorption of approximately 18%. The clay used was pulverized and an amount sufficiently large for the series of experiments was thoroughly mixed, so as to assure uniform distribution of the scum-forming minerals. Both the clay and, of course, the proportioned terra cotta body later developed the green discoloration. All trial bodies were thoroughly pugged so that whatever counteracting agent was employed, it would be distributed throughout the mass. Cones with a base diameter of about two inches and an altitude of about four inches were pressed from each mixture. These cones were slowly dried, fired at cone 4 in muffle terra cotta kilns, and then set in shallow enameled pans in about one-half inch of water. The water is thus drawn up through the porous cone by capillary attraction and evaporates from the upper surface, concentrating the majority of the scum on the point of the cone, and thus making identification easier.

It was soon discovered that if cones were dipped in a solution of C. P. HCl, the scum would rapidly turn to a reddish brown, and then gradually to a deep black-green color. Possibly this is due in the first color change to the formation of red vanadium tetrachloride, VCl_4, and brown pyrovanadic acid, $H_4V_2O_7$, and later to the formation of divanadyl tetrachloride, $(VO)_2\ Cl_45H_2O_7$, a dark green salt. Red molybdenum trichloride, $MoCl_3$, and brown molybdenum tetrachloride, $MoCl_4$, and to some extent the ferric chlorides, brown or black $FeCl_3$ or reddish yellow $FeCl_36H_2O$, may also enter into the first reaction. The formation of green nickel chloride, $NiCl_26H_2O$, may be part of the second reaction. This serves as a more or less delicate test for the presence of the green salt, making it readily apparent on test pieces which would otherwise be classed as scum free. Where there is only a very small amount of scumming the first color change will not be noticeable, but the green discoloration will gradually appear.

In the experiments both the insoluble basic carbonate and the soluble acetate of lead were tried as scum preventatives. The following amounts of white lead were added to a definite weight of terra cotta body and made into cones as described above: 0.2, 0.4, 0.6, 0.8, 1.0, 1.6, and 3.2%. Lead acetate was likewise added in amounts of 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, and 3.2%. It is evident from these tests that the lead salts are increasingly effective as preventatives of green scum formation. However, even with the highest per cents used, a slight amount of scumming is noticeable after prolonged soaking and drying, and dipping of points of cones in HCl solution. It is also evident that white lead and lead acetate are about equal in hindering power. There is much less poison hazard, of course, in the use of white lead. In this reaction an insoluble lead vanadate is evidently formed. This agrees with Thorpe,[1] who states that the pyrovanadates of the heavy metals are mostly insoluble.

These laboratory tests of the use of lead salts in green scum control are also borne out by trial in a large way.

Use of Bismuth Referring to the last quotation from Thorpe's Dictionary of Applied Chemistry, it was thought that the salts of bismuth (atomic wt. of $Bi = 208$) might act similarly to lead. Tests using 0.2, 0.4, 0.6 and 1.6% of bismuth nitrate in same body as above, indicate that bismuth will also hinder the development of the green scum. With 1.6% of this salt, the cones after prolonged soaking, drying, and dipping in HCl solution, show a very slight amount of discoloration. The use of bismuth salts has not been tried in a larger scale, but has been experimented with only on a laboratory scale. The cost of the ordinary bismuth salts makes their use entirely prohibitive in a commercial way.

Use of Antimony and Zinc Antimony and zinc compounds have been tried in same manner as white lead and bismuth nitrate, but do not hinder scum development.

2. Dipping

The other method of prevention mentioned, by dipping individual pieces, is only applicable to certain types of ware.

In Potassium Carbonate Probably the salt most generally used is potassium carbonate. Brick dipped in a solution of this salt do not ordinarily green scum, but there seems to be a few cases where scumming has occurred. Whether the exceptions to the rule are due to the personal equation which enters into all manufacture, it is impossible to say.

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[1] *Loc. cit.*, p. 611.

In Barium Chloride The same result has been accomplished in the laboratory using solutions of barium chloride, calcium chloride, and sodium carbonate. These solutions, however, in the same concentration as the potassium solution used, in turn tend to cause the formation of a white scum.

It would seem, however, that the use of potassium carbonate is open to objection on the ground that potassium sulphate, one of the products which results in the reaction, is itself soluble. No table at hand gives the solubility of vanadium carbonate. The ideal condition should be when insoluble products are formed in the chemical reaction taking place when dipping in a given solution. Apparently a solution of a soluble barium salt and an ammonium salt should fulfill these conditions. The barium will precipitate the soluble sulphates as insoluble barium sulphate. The ammonium salt, if the conditions are right, will precipitate the vanadium as white difficultly soluble ammonium metavanadate. The addition of barium chloride or barium hydroxide to a solution of the scum under investigation causes the formation of a white precipitate. A white precipitate forms when ammonium hydroxide is added. Also the solution loses its green color.

A solution of 30 grams barium chloride and 30 grams ammonium chloride to one gallon of water has so far proved effective in our tests. One-half of several brick known to develop scumming were dipped in the above solution. The brick were then set in a pan in about one-half inch of water. After several days the dipped half of each brick was free from green scumming while the undipped half scummed copiously. The same results have been observed with the use of a barium chloride, ammonium hydroxide solution. What the results will be when bricks so treated are set to weather through a winter season, have not yet been determined.

The Removal and Prevention of the Reappearance of Green Scumming Caused by Vanadium

A little laboratory work has been done on this problem, but so far no method has been developed which is satisfactory. The use of solutions acidified with sulphuric or hydrochloric acid, for cleaning, tend to form undesirable compounds and are to be avoided for this reason, and also because they attack the mortar joints of the walls to be cleaned. A potassium carbonate solution sprayed on a wall which has green scummed is said gradually to cause the green color to disappear.

Undoubtedly an understanding of the various methods of cleaning green stained walls, and preventing subsequent discoloration, would be a welcome addition to the knowledge of many of the industry.

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ORIGINAL PAPERS

INVESTIGATION ON ENAMEL CLAYS[1]

By V. W. Boeker

ABSTRACT

Functions of clay in enameling and requirements of enamel clays are enumerated. The investigation deals with twelve representative enamel clays, which were examined for water of plasticity, drying shrinkage, modulus of rupture and properties when fired to 1000°C. Using these clays in enamel slips, viscosity, suspension test, and hydrogen-ion concentration by the indicator method were run. Fineness test, petrographic examination and chemical analyses were made on the clays. They were then tested in a cover coat enamel, subjecting the test pieces to impact test and thermal shock. The results of all the tests are summarized and conclusions drawn therefrom.

Introduction

The purpose of this investigation was to find the relation between the properties of several clays and their action in the enameling of sheet metal processes, and if possible, to establish a uniform and practical test for determining the suitability of clay for such a use.

Functions of Clay in Enameling

The addition of clay to enamels serves several purposes, namely:

1. To introduce alumina with silica.

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[1] This material was gathered in connection with the preparation of a thesis to fulfil the partial requirements for the degree of Bachelor of Science in Ceramic Engineering University of Illinois. Recd. April 27, 1926.

2. As a floating agent to hold the non-plastic material in suspension; without such an addition the non-plastic would settle rapidly in dipping tanks.

3. To give the enamel slip the proper viscosity to prevent it from flowing excessively on inclined surfaces after dipping. This is obviously very necessary, inasmuch as the sheet metal is non-absorbent.

4. To serve as an adhesive, whereby the non-plastic particles will adhere to the metal shapes after drying before firing. A high degree of adhesion is absolutely necessary because of slight shocks and abrasions to which the dipped articles are subjected, notwithstanding the great care which is taken in protecting the same.

5. A portion of the clay enters into chemical reaction with the enameling batch and according to Grunwald it promotes chemical reactions with various metallic oxides and the silica. The portion of clay which is not taken into solution as well as that which goes into solution acts in a general way as a refractory, affording a convenient means for control of this property of the enamel.

6. The undissolved and finely divided clay in suspension contributes to the opacity of the enamel.

7. The alumina in clay is found to increase the tenacity and viscosity, and also to minimize the injurious effects of too rapid cooling. Landrum states that the addition of clay adds to the stretching qualities of enamel coatings which he explains as due to "the infusibility of clays, which property keeps it from entering into complete combination with other material. Instead, it holds apart the glass mass with which each particle of clay is surrounded during the contraction of the steel and allows it to pull away from it without chipping when expanded."

Requirements of Enamel Clay

Our knowledge of the requirements to be met by clay suitable for use in the preparation of enamel is not satisfactory. J. B. Shaw,[1] has made a comparison of several enamel clays with reference to their capability of floating enamel frits. H. F. Staley[2] has enumerated some of the requirements which should be met by a clay selected for such a purpose. These properties have to do with the following: color, plasticity, purity, with respect to freedom from oil, carbonaceous matter, etc.

Grunwald in "Raw Materials of the Enamel Industry" has stated that the composition of the best clay for such a purpose should lie within the following limits: 51–55% silica, 31–34% alumina and iron content less than 1% with complete absence of calcium carbonate. Also, he states that the behavior of clay when heated to the firing temperature is of importance.

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[1] *Trans. Amer. Ceram. Soc.*, **19**, 339 (1917).

[2] Bur. Stand., *Tech. Paper*, No. 142.

Materials

In considering what clays to study in this investigation it was thought advisable to include only those clays that were being used in the enameling industry, in order that no time should be wasted in testing unsuitable materials.

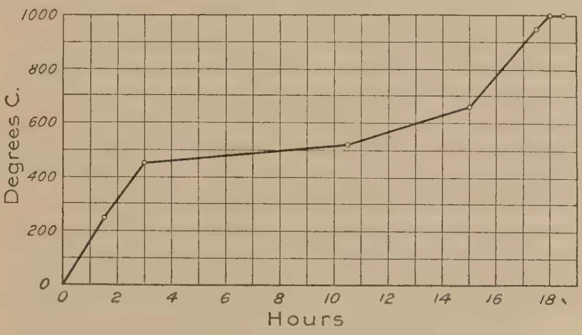

FIG. 1.

The clays selected here are fairly representative of almost every kind of clay used in enameling. Each clay is here given a number and will always be referred to by that number throughout this discussion.

No. 1.—Special enamel "A" clay
No. 2.—Special enamel "B" clay
No. 3.—Special enamel "brown" clay
No. 4.—Clay from Anna, Illinois
No. 5.—Clay from Mayfield, Kentucky
No. 6.—"F" clay
No. 7.—"E.B." clay
No. 8.—"V" clay
No. 9.—"C.C." clay
No. 10.—"O" clay
No. 11.—German enameler's fat clay
No. 12.—English clay

For the purpose of getting useful results typical commercial enamel frits were used. These frits, for both ground and cover coats, were produced under normal operating conditions in a plant smelter.

The steel was one of the better grades of sheet steel commonly used in commercial practice.

Experimental Work

Throughout this investigation it was constantly kept in mind that, in order to get useful results, only such tests could be employed as could easily be reproduced in a plant laboratory. The tests were, therefore, conducted in the most simple manner possible and with a minimum amount of special laboratory equipment.

Wherever possible the tests were carried out according to the standard methods of the AMERICAN CERAMIC SOCIETY. These methods will merely be referred to later but will not be discussed in this paper; however, in any case not covered by some standard, or where a more direct and less complicated method than the standard was thought to be desirable, the experimental method will be discussed in more detail.

Preparation The clay as received was run through a small jaw crusher and then through a set of smooth rolls, which were adjusted to reduce the size of the clay particles to approxi-

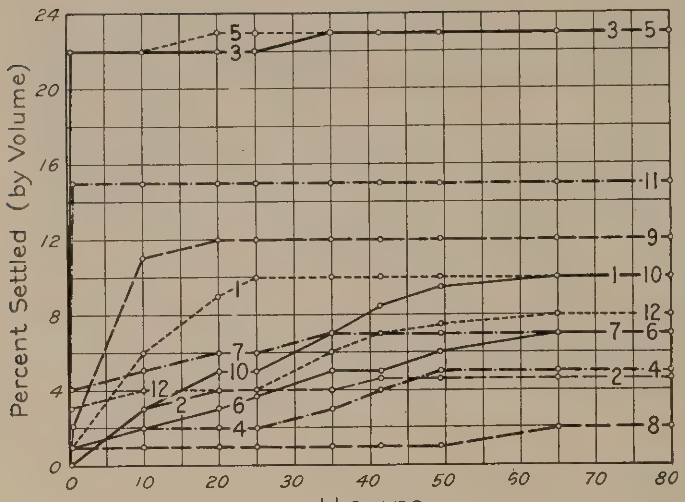

FIG. 2.

mately 20-mesh. The pulverized material was then very thoroughly mixed and a small sample taken for chemical analysis.

Clay Tests These included an examination for the water of plasticity, drying shrinkage, and modulus of rupture. The results were as follows:

TABLE I

CLAY TESTS

Clay. no.	Av. modulus of rupture (lbs./sq. in.)	Av. water of plasticity (% dry wt.)	Av. drying shrinkage (% dry vol.)	Clay no.	Av. modulus of rupture (lbs./sq. in.)	Av. water of plasticity (% dry wt.)	Av. drying shrinkage (% dry vol.)
1	194.5	42.3	33.23	7	267.2	41.2	29.8
2	176.1	34.8	23.8	8	192.5	22.9	35.1
3	270.9	41.9	33.1	9	66.8	37.4	13.9
4	236.6	41.3	35.1	10	126.5	43.5	27.5
5	200.3	35.3	27.1	11	285.4	31.1	30.7
6	284.2	24.4	39.5	12	356.4	35.6	32.9

It was deemed advisable to investigate the properties of these clays when fired to a temperature of 1000°C. This represents about the maximum temperature to which these clays are subjected in commercial practice.

The test pieces used in drying shrinkage and modulus of rupture tests, after thorough drying were placed in a small laboratory gas-fired muffle furnace and fired as shown in the graph in Fig. 1. Every precaution was taken to get an even distribution of heat so that each test piece would get the same heat treatment. Several thermocouples placed within the stack of test pieces served as a constant check on the temperature and a guide to regulate the heat distribution.

After cooling, the pieces were carefully inspected and their firing shrinkages and porosities were determined. The results were as follows:

TABLE II

Clay no.	Av. firing shrinkage (% dry vol.)	Av. apparent porosity at 1000°C	Clay no.	Av. firing shrinkage (% dry vol.)	Av. apparent porosity at 1000°C
1	13.2	42.1	7	10.5	42.3
2	6.2	38.0	8	8.8	34.6
3	11.2	40.7	9	8.9	43.6
4	13.4	37.1	10	18.4	42.3
5	6.4	37.6	11	9.9	29.6
6	14.3	35.4	12	29.6	33.0

General Condition and Color of Fired Test Piece—Remarks

No. 1.—Slightly cracked. A dirty white with a slight tinge of pink.

No. 2.—A good white. Safe firing conduct.

No. 3.—Safe firing. A decided pink color.

No. 4.—Slightly cracked. A dirty white.

No. 5.—Safe firing. A good white.

No. 6.—A few large cracks developed. A dirty white with a tinge of brown.

No. 7.—Safe firing. A fair white.

No. 8.—Safe firing. Dirty gray or buff color.

No. 9.—Many long cracks developed. A fairly good white.

No. 10.—Many long cracks developed. Almost a pure white with a slight tinge of pink.

No. 11.—Safe firing. Buff color.

No. 12.—Safe firing. Almost a pure white with a slight tinge of pink.

Viscosity The enamel slip used in this determination consisted of 100% frit, which had been ground to pass an 80-mesh screen, 10% clay and 63.5% water. No flocculating agent was used. The materials were weighed, placed in pint jars and tightly sealed. These were then placed in a shaking machine and run for a period of four hours. At the end of this time all the mixtures had been worked into good smooth slips.

Exactly 100 cc. of each of these slips was run through a constant flow viscosimeter with a $\frac{3}{16}$-inch opening, and the time required for this accurately noted. The viscosimeter itself was standardized against pure water at 15°C. The results are shown in the following table:

TABLE III
RELATIVE VISCOSITY
(Water = 1)

Clay no.	Sp. gr.	Viscosity	Clay no.	Sp. gr.	Viscosity
1	1.46	1.54	7	1.63	1.81
2	1.61	68.0	8	1.63	2.48
3	1.63	1.79	9	1.61	1.89
4	1.75	1.51	10	1.57	1.89
5	1.59	1.80	11	1.62	2.34
6	1.56	1.86	12	1.57	1.45

Suspension Test In order to determine how the clays would act when used to hold the frit in suspension in the enamel slip for a period of time, exactly 100 cc. of each of the slips prepared under "viscosity test" were poured into a weighed 100 cc. graduated cylinder, and let stand undisturbed. The amount of clear water and the amount of cloudy clay slip above the blue enamel mixture were noted at frequent intervals until the total amount of settle had become constant in all of the tubes. This required a period of eighty-one hours.

Figure 2 shows the results of this test graphically in terms of the total amount of settle.

Table IV

Suspension Test

Clay No. (in % vol. cc.)

Time in hrs.	% by vol.	1	2	3	4	5	6	7	8	9	10	11	12
1.5	H_2O	–	–	–	1	–	1	–	1	–	–	–	–
	Clay	–	–	22	–	–	–	–	–	–	–	–	–
11	H_2O	3	3	2	1	3	1	2	1	11	6	2	1
	Clay	–	–	20	1	19	1	3	–	–	–	13	3
20	H_2O	5	4	4	1	5	2	2	–	12	9	3	2
	Clay	–	–	18	1	18	1	4	1	–	–	12	2
25	H_2O	5	4	4	1	5	3	2	–	12	10	3	2
	Clay	–	–	18	1	18	1	4	1	–	–	12	2
35	H_2O	7	4	5	2	6	4.5	3	–	12	10	3	4
	Clay	–	–	18	1	17	.5	4	1	–	–	12	2
43	H_2O	8.5	4	5	3	7	4.5	3	–	12	10	3	4
	Clay	–	–	18	1	16	.5	4	1	–	–	12	3
49	H_2O	9.5	4.5	5	4	7	6	4	–	12	10	3	4
	Clay	–	–	17	1	16	–	3	1	–	–	12	3.5
65	H_2O	10	4.5	6.5	4	7.5	7	4	1	12	10	3	5.2
	Clay	–	–	16.5	1	15.5	–	3	1	–	–	12	2.5
81	H_2O	10	4.5	7	4	8	7	4	1	12	10	3	6
	Clay	–	–	16	1	15	–	3	1	–	–	12	2

Hydrogen-ion Concentration

The ability of the clay to hold the non-plastic particles of the enamel frit in suspension is largely governed by the amount of flocculation or deflocculation of the clay particles. It was thought that the degree of dispersion of the clay particles was dependent upon the degree of acidity or alkalinity of the slip, and that, therefore, the hydrogen-ion concentration would be a governing criterion of the clay's suspending power.

The indicator method was selected for this determination as it does not require the use of any special or complicated equipment. Other distinctive advantages of this method are the ease and rapidity with which the approximate ion concentration of a solution may be measured. The method used was that of Michaelis and Geymant as given in Clarks "Determination of the Hydrogen Ion."

The stock solutions used were as follows:

1. 2, 4 dinitro phenol 0.05% aqueous solution
2. 2, 5 dinitro phenol 0.025% aqueous solution
3. *p*-nitro phenol 0.1% aqueous solution
4. *m*-nitro phenol 0.3% aqueous solution

To test tubes of the same diameters was added seriatim the volumes of the indicator solutions given in the following tables, the indicator solutions being prepared by diluting the stock solutions (given above) ten times with soda solution.

m-nitro phenol

Tube number	1	2	3	4	5	6	7	8	9
Cc. of indicator	5.2	4.2	3.0	2.3	1.5	1.0	0.66	0.43	0.27
*p*H	8.4	8.2	8.0	7.8	7.6	7.4	7.2	7.0	6.8

p-nitro phenol

Tube number	1	2	3	4	5	6	7	8	9
Cc. of indicator	4.05	3.0	2.0	1.4	0.94	0.63	0.4	0.25	0.16
*p*H	7.0	6.8	6.6	6.4	6.2	6.0	5.8	5.6	5.4

2, 5 dinitro phenol

Tube number	1	2	3	4	5	6	7	8	9
Cc. of indicator	6.6	5.5	4.5	3.4	2.4	1.65	1.1	0.74	
*p*H	5.4	5.2	5.0	4.8	4.6	4.4	4.2	4.0	

2, 4 dinitro phenol

Tube number	1	2	3	4	5	6	7	8	9
Cc. of indicator	6.7	5.7	4.6	3.4	2.5	1.74	1.2	0.78	0.51
*p*H value	4.4	4.2	4.0	3.8	3.6	3.4	3.2	3.0	2.8

The value of *p*H is equal to the negative log of the hydrogen-ion concentration. The test tubes were sealed with paraffined corks and when not in use were protected from direct light.

Twenty-five grams of each clay and 50 cc. of water were placed in large test tubes and the mixtures agitated until all of the clay was in suspension, and then allowed to stand for a few days until the clay settled. The supernatant liquid was decanted through a filter paper to get an absolutely clear solution.

This did not work successfully, however, in all cases. After standing one week the slip made up with clay No. 5 showed no clear water on top of the clay. All attempts to obtain a clear solution by means of filtration failed. A clear solution was finally obtained by passing the slip through a high speed centrifuge several times. In the slip made up with clay No. 12, the clay settled to the bottom of the tube after a few days, but the supernatant liquid would not filter to a clear solution. Here, again the centrifuge was successful in removing the colloidal matter in the solution.

To six cc. of the clear solutions obtained from the clay slips one cc. of the indicator solution was added and the solution compared with the standards given below.

HYDROGEN-ION CONCENTRATION

Clay no.	*p*H	Clay no.	*p*H
1	6.0	7	6.0
2	4.4	8	4.0
3	4.2	9	6.2
4	6.5	10	6.4
5	5.8	11	6.6
	4.0	12	6.4

Fineness of the Material No attempt was made in this investigation to determine by elutriation the actual size of the clay particles. A screen test was run to determine the kind and amount of the impurities contained in the clay. It was found that most of the impurities in these clays were extremely small in size, so to save time only one screen was used. One hundred grams of the dry clay were placed on a 300-mesh screen and thoroughly washed with water. All the clay particles were thus washed through the screen while the coarser grained impurities were retained. This residue was examined and weighed after drying to constant weight at 110°C.

Fineness Test

Clay no.	% residue on 300-mesh	Residue
1	0.35	Fine dark sand. Few small chips of carbonaceous material
2	1.5	Very fine. Seemingly pure quartz
3	5.7	Fine dark sand. Few pieces (about ¼ in. diameter) of quartz
4	1.3	Fine dark sand. Few pieces (¼ in. diameter) of an opal-like mineral
5	2.25	Fine dark sand with few small particles of lignite or coal
6	1.42	All fine sand
7	9.4	Some fine dark sand. Mostly black, coal-like material
8	8.6	All very fine sand
9	0.45	Some fine sand. Mostly very fine mica (flaky)
10	1.95	Some fine white sand. Mostly very fine mica
11	1.1	Fine, dark sand
12	1.45	Fine sand. Few small particles of carbonaceous material

Report of Petrographic Examination of Certain Clays Made by the Bureau of Mines[1]

No. 2. Composed of quartz clay aggregates carrying a little sericite and a few tiny rutile needles. The quartz is finely divided. Other accessory minerals are rare. Similar to No. 12.

No. 3. The coarse separate shows considerable variety of associated minerals such as hornblende, tourmaline, zircon, rutile, biotite. Characterized also by a large amount of quartz (silt size) and sericite muscovite, also by the presence of particles of glass (possibly pulverized frit).

Clay separate somewhat similar but contains a much larger amount of sericite and less quartz. The clay mineral is brownish in color and encloses as an aggregate, small particles of sericite, quartz, limonite, and rutile. The great variety of associated minerals and abundance of quartz in silt would indicate a close similarity to certain slip clays.

No. 6. The clay aggregate contains small amounts of quartz and sericite. Rather a clean sample of clay and free from most accessory minerals. Kaolin crystalline but without crystal outline.

No. 8. Characterized by the presence of a variety of accessory minerals and of abundant quartz in coarser (sand) sizes as well as fine silt, quartz, zircon, rutile, tourmaline, primary kaolin, sericite, glass as referred to under No. 3 and (rarely) muscovite.

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[1] This petrographic examination of the clays was made through the courtesy of the Superintendent, G. A. Bole, Columbus, Ohio.

No. 12. Rather uniform in composition and consisting of quartz-clay aggregates carrying tiny rutile needles and a small amount of sericite. Other accessory minerals not present to any extent. Similar to No. 2.

In Nos. 3 and 8 there has been noted the presence of fragments of glass. The surface of this glass is often crazed and cracked. The rather constant occurrence of this glass in some samples and its entire absence in others is significant. It is possible that this has been a mill admixture or it might be an accidental surface contamination in the mill bin. It may possibly be a fritted enamel. It is hardly likely that this glass occurs naturally in the clays.

Chemical Analysis

Chemical analyses of the clays were made from representative samples of the materials used in this investigation by a competent commercial analyst.

Clay no.	2	3	12
	%	%	%
Silica	53.86	48.32	57.68
Iron and alumina	31.90	35.94	31.06
Calcium oxide	.20	1.26	.44
Magnesium oxide	.12	.56	.16
Loss on ignition	11.18	13.64	9.06
Alkalis (by difference)	.14	.28	1.60

Clay no.	6	8
	%	%
Silica	47.01	57.68
Alumina	34.19	28.25
Iron	.81	1.17
Calcium oxide	.38	.21
Magnesium oxide	.46	.29
Alkalis (by difference)	2.67	2.30
Loss on ignition	14.48	10.10

Enamel Tests

In order to secure uniformity, the frits were first ground dry in small porcelain ball mills and screened at intervals frequent enough to produce nearly uniform size particles. The ground coat frits were passed through an 80-mesh screen and the cover coats through a 100-mesh.

A thin uniform coating of the ground coat was applied to small test pieces, 2 x 4 inches, which had previously been scaled and pickled in the usual manner. These were fired under uniform conditions to produce a good, well-fired base for the cover enamels.

The clays were then tested in a series of cover coats made up as follows: frit, 100%, clay, 7%, tin oxide, 4%, leukonin, 3%, and water 40% (approximately).

A uniform coating of the cover enamel was applied to the test pieces and they were at once placed in a small oven kept at a constant temperature of 110°C. When thoroughly dry they were fired in a small gas-fired muffle furnace for 2.5 minutes at 960°C. All of the test pieces were fired under exactly the same conditions.

The finish coat enamel was applied in the same manner. The test pieces were then fired for 2 minutes at 950°C. Again, the firing conditions were kept constant.

The condition of the enamel slip and its suitability for dipping were noted, also the amount of running or flowing of the enamel on the test piece. The fired pieces, both first coat white and finish coat, were carefully examined for any defects and compared as to color, gloss, opacity, etc.

Besides these general examinations and comparisons, two other tests were made on all the finished pieces.

Enamel Tests

General Condition of Enamel Slip

1. A good smooth slip. Stays in suspension
2. Same as No. 1. A pure white slip
3. A poor slip. Settles to bottom very rapidly
4. Fair slip
5. Settles quite rapidly. Flows considerably on test piece, causing beading on edges
6. A good slip. Stays in suspension well
7. A poor slip. Settles quite rapidly
8. A smooth white slip. Settles slowly
9. A good white. Stays in suspension well
10. A good white. Stays in suspension well
11. A good slip. Stays in suspension well
12. A good slip. Stays in suspension well

General Condition of Test Pieces

First Coat White

1. Good, smooth, matured enamel
2. Good, smooth, matured enamel
3. Pieces completely covered with bubbles. Enamel in so poor a condition that second coat white could not be applied
4. Immature enamel. Not smooth, due to clay which had risen to surface
5. Same general condition as No. 4
6. A good, smooth, matured enamel
7. Matured, but rough. Test pieces contain many pin holes and minute bubbles
8. Good, smooth, matured enamel
9. Somewhat underfired and rather dull
10. Slightly underfired and rather dull
11. Very good enamel
12. Very good enamel

Finish Coat White

1. An immature, dull enamel
2. A good smooth enamel. Rather dull
3. (It was not possible to apply the second coat enamel to this series. See above)

4. Seemingly immature and rough, due to clay which has risen to surface. However, in small spots not covered by clay, enamel has a good gloss.
5. Same general conditions as No. 4
6. A good enamel with a fair gloss
7. Very poor enamel. Many pin holes and small black specks in enamel
8. A good enamel with a good gloss
9. A smooth enamel, but rather immature and dull
10. Same general conditions as No. 9
11. A very good enamel, with an excellent gloss
12. About the same as No. 11

If the better enamels were arranged according to their gloss and maturity, placing the best one first, the order would be as follows: Nos. 11, 12, 8, 6, and 2.

Not enough difference could be noted in the opacity of the better enamels to make any comparison.

1. Impact Test This test was carried out according to the Bureau of Standards method and with apparatus suggested by the Bureau.

IMPACT TESTS (Ft.–lbs.)

Clay no.	Test 1	Test 2	Test 3	Average	Clay no.	Test 1	Test 2	Test 3	Average
1	0.325	0.35	0.35	0.342	8	0.30	0.275	0.275	0.283
2	0.325	0.30	0.40	0.348	9	0.225	0.25	0.225	0.342
4	0.275	0.275	0.275	0.275	10	0.225	0.25	0.225	0.225
5	0.25	0.225	0.25	0.242	11	0.30	0.30	0.275	0.292
6	0.25	0.225	0.25	0.242	12	0.30	0.275	0.275	0.317
7	0.175	0.175	0.20	0.183					

2. Thermal Shock The finished test pieces were placed in a small electrical resistance furnace and heated to 125°C. After allowing them to remain in the furnace long enough to come to a uniform temperature they were removed and immediately quenched in water at 15°C. This procedure was repeated five times at this temperature and at increasing temperature intervals of 25°C. Failure was accepted when the enamel chipped off of the piece. A small chip on the edge of the piece where the enamel was somewhat beaded was not accepted as failure.

THERMAL SHOCK TEST

	Slightly crazed		Crazed		Failure			Slightly crazed		Crazed		Failure	
Clay	Test	Temp.	Test	Temp.	Test	Temp.	Clay	Test	Temp.	Test	Temp.	Test	Temp.
1	2	225°C	4	250°C	2	350°C	7	–	–	–	–	2	200
2	1	275	1	300	3	350	8	1	250	1	300	2	350
3	–	–	–	–	–	–	9	3	225	1	275	2	325
4	1	275	1	300	5	350	10	2	225	1	275	3	350
5	–	–	1	225	1	300	11	–	–	–	–	2	200
6	1	225	1	275	4	300	12	–	–	1	225	5	325

Summary of Results

A careful examination of the above results clearly shows many of the functions of the clay in the enameling process, and also discloses some of the relations existing between the properties of the clay and its effect upon the finished enamel.

The suspension test is, seemingly, not a good criterion of the ability of the clay to hold the enamel in suspension in the dipping process. The results found in the suspension test do not agree with those found in the enamel slips used in this work.

It is also noted that the results of the suspension test do not check with the hydrogen-ion concentration of the clays. In general, however, the hydrogen-ion concentration of the clays does agree with the results obtained in the enamel slips. All of the clays, whose *p*H values are greater than 6.0, proved to be good suspension agents for the cover coat enamels. It cannot be said, however, that clays having *p*H values of less than 6.0 are not good floating agents, as some of the clays having *p*H values lower than this kept the slip in suspension very well during the dipping process.

From the results of the screen test, it seems that the quality of the impurities in the clay is of much more importance than the quantity. While the amount of the impurities in the clays giving the best enamels varied greatly, there is no great difference noted in the quality of these materials. All of them, *i.e.*, those giving best enamels, Nos. 2, 6, 8, 11, with the exception of No. 12, contained only fine sand as an impurity. In No. 12 a small amount of carbonaceous matter was also found. It is further noted that No. 7 which contained considerable carbon in the form of coal or lignite, failed completely by the firing of these particles in the muffle, with resulting pin holes and bubbles in the enamel.

Of the clays analyzed in this investigation, those giving the best enamels (2, 6, 8, and 12) favorably agree in their chemical analysis. The small amount of CaO in these clays seems to have no effect upon the resulting enamel. No. 3, however, which has a much larger content of CaO, failed completely on account of the decomposition of the $CaCO_3$ in the muffle after the enamel had become viscous with resulting blistering of the enamel.

The brilliancy and degree of maturity of the finished enamel is directly related to the porosity of the clay at 1000°C. If the enamels are placed in order according to their luster, placing the best one first, and the clays placed in the order of their increasing porosities, the two are found to be identical. The objection may be raised that samples No. 4 and 5 should give fairly good enamels according to this classification. The reason for these enamels not having a good glossy appearance is that the clay rose to the surface in drying and formed a thin, dull coating over the enamel when fired. It is to be noted that the results show that these enamels did have a good gloss in small spots not covered by the clay.

The resistance of the enamels to impact and thermal shock is greatly affected by the clay. A comparatively low impact caused some of the enamels to fail, while others resisted impact forces of nearly twice that amount. A study of the results of the thermal shock test show a variation of 150°C in the failing temperatures of the different enamels. These differences are not due to any difference in the maturity of the enamels. No relation was found, however, between any of the properties of the clays and their influence upon the strength and elasticity of the enamels.

Conclusions

It is evident that the exact degree to which the clay affects the properties of a finished enamel is dependent upon the composition of the enamel.

1. The suspension test, alone, cannot be used as a measure of the ability of a clay to float the enamel in the dipping process.

2. A knowledge of the character of the impurities contained in the clay is of as much value in judging the suitability of a clay for enameling purposes as the quantity of these impurities.

3. A small amount of carbonaceous material in the clay does not affect the enamel, unless this be present in the form of coal or lignite.

4. Finely divided calcium carbonate in the clay, in amounts less than 0.5% CaO, has no harmful effect upon the enamel. If the CaO content is greater than 1% it will cause the enamel to blister.

5. The degree of maturity and the luster of the finished enamel is inversely proportional to the increasing porosities of the clays at 1000°C.

6. The strength of the finished enamel and its ability to resist thermal shocks is greatly affected by the clay used.

7. This investigation has shown that the clay used in compounding the mill-batch of enamels may be detrimental or beneficial in its effects upon the essential properties of the finished enamel, depending upon the clay used. It has been shown that the clay affects the maturing temperature, texture, luster, strength, and elasticity of the finished enamel.

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THE ATTACK OF ARSENIC COMPOUNDS ON FIRECLAY REFRACTORY MATERIAL[1]

By W. E. S. Turner

ABSTRACT

McSwiney's statement regarding arsenic compounds being responsible for rapid corrosive action on tank blocks is discussed. It is pointed out that if arsenic compounds exert a marked corrosive action on fire clay, it should be demonstrated by an increased iron oxide or alumina content, or both, in the resulting glass. Data collected in experiments run is presented, which contradicts McSwiney's statement. Only when arsenic in excess of the amount used ordinarily is present in glasses melted at temperatures of 1450 and 1500°C, or above ordinary working temperatures, can corrosion due to arsenic be traced. A full discussion of corrosion of glass house refractories, effects of colors on the heat conductivity of glasses at high and low temperatures, and variations between the types of glasses referred to in Dr. Turner's paper and in McSwiney's, is presented by McSwiney.

In a recent paper published in this *Journal*, D. J. McSwiney discussed a matter of very great interest to manufacturers of glass prepared in tank furnaces, namely, the rapid corrosion of tank blocks and the influence on this rate of corrosion by the use of selenium and of arsenious oxide. He came to the conclusion, quite rightly in my view, that selenium in itself is not to be regarded as a corrosive agent, but he brought forward a certain amount of general evidence which led him to the conclusion that the use of arsenious oxide is responsible for the corrosive action observed. For example, McSwiney considered the relative life of tank furnaces melting, in the one case colorless glass, and in the other green glass, and instanced a furnace melting green glass in which the average tank life diminished from 14 months to approximately 6½ after the addition to the batch of 5 pounds of arsenious oxide per ton of sand.

There is a certain amount of *a priori* evidence suggesting that compounds of arsenic might be regarded as corrodents, as also are some of the compounds of nitrogen and more particularly of phosphorus, elements occurring in the same periodic group, and, therefore, having compounds of somewhat analogous properties. Arsenic compounds, indeed, very readily attack and corrode platinum. Phosphoric oxide at a temperature of 400° or higher attacks both glass and fused silica.

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[1] The investigations from which the data given in this paper were derived were carried out in the years 1922–24 on behalf of the Glass Research Association and this paper is now published with the permission of that body and of the Department of Scientific and Industrial Research. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Glass Division). Received May 1, 1926.

[2] D. J. McSwiney, "The Action of Arsenic Compounds on Tank Block," *Jour. Amer. Ceram. Soc.*, 8[5] 307–309(1925).

The alkaline nitrates which melt and probably react at a lower temperature are more corrosive of fireclay pots than are the corresponding carbonates. Phosphate glasses are generally recognized by glass manufacturers as being among the comparatively corrosive glasses. These facts at least suggest that arsenic compounds might likewise be destructive of fireclay vessels.

The evidence which McSwiney deduces in support of his view that arsenic compounds exert a corrosive action may, however, be capable of a different interpretation from that which he gives. In any case, the statement that arsenic compounds exert a specially active corroding action on fire clay can best be tested by direct determination, and investigations which have been in progress here during the past three to four years enable me to make a contribution to the elucidation of the problem.

The experiments, the results of which are collected in Tables I, II, and III, were carried out on a soda-lime-silica glass of composition similar to that commonly melted for colorless glass in tank furnaces. The glass referred to in Table I was melted from the batch: sand 1000, soda ash 370, limestone (calcium carbonate) 200.

In the experiments to which Tables II and III refer, the batch had the composition: sand 1000, soda ash 325, limestone (calcium carbonate) 228.

In the experiments on the first-named glass, meltings were carried out under precisely comparative conditions in small fireclay crucibles and increasing amounts of arsenious oxide were added to the batch. If arsenic compounds exert a marked corrosive action on fire clay it should be demonstrated by an increase in the iron oxide content, or the alumina content, or both, of the resulting glass, since these oxides would be derived to an increasing extent from the fire clay as the result of the corrosion. In Table I the results are recorded of the amount of iron oxide present in the glass resulting under the conditions stated. In experiments 5 to 9, namely, those in which the glass was melted at

TABLE I

Experiment no.	Melting temperature	Oz. of arsenic per 1000 lb. of sand	Per cent Fe_2O_3 in the glass
1	1400°	Nil	n. d.
2	1400	5	0.06
3	1400	10	0.06
4	1400	25	0.05
5	1370	Nil	0.05
6	1370	10	0.04
7	1370	25	0.04
8	1370	100	0.03
9	1370	150	0.03

1370°, the amount of arsenic in the batch varied from 0 to 150 ounces per 1000 pounds of sand; that is, it rose to amounts in great excess of those used in tank furnace practice where it is seldom that as much as 50 ounces are employed. It will be noted that the percentage of iron oxide present instead of showing a marked increase is actually less in the case of the batch containing most arsenious oxide. In both sets of experiments, in fact, there appears a tendency to diminution which is contrary to the view that increased corrosion occurs with the addition of arsenic compounds.

Table II

1	2	3	4	5	6	7	8
Glass No.	Pot size, make, and number	Order of melting in pot	As_2O_3 in batch per 1000 lbs. sand (ounces)	Calcd. As_2O_3% in glass	Observed As_2O_3 % in glass	Al_2O_3% in glass	Fe_2O_3% in glass
527 M	50 lb. (*Wa*)	4	16	0.18	0.07	0.27	0.06
527 P	50 lb. (*Wb*)	3	32	0.15	0.17	0.28	0.06
P/2	100 lb. (*Wc*)	2	32	0.15	0.16	0.32	0.04
P/3	100 lb. (*We*)	1	32	0.15	0.14	0.17	0.05
527 N/2	100 lb. (*Wc*)	3	48	0.23	0.20	0.21	0.05
527 N/3	100 lb. (*We*)	2	48	0.23	0.19	0.13	0.05
527 N/4	50 lb. (*Ma*)	3	48	0.23	0.20	0.16	0.05
527 O	50 lb. (*Wb*)	2	72	0.34	0.38	0.41	0.09
O/2	100 lb. (*Wd*)	3	72	0.34	0.37	0.34	0.06
O/3	100 lb. (*We*)	3	72	0.34	0.31	0.26	0.04
527 Q	50 lb. (*Wb*)	4	120	0.57	0.55	0.17	0.05
Q/3	100 lb. (*We*)	4	120	0.57	0.48	0.13	0.05
527 R	50 lb. (*Ma*)	4	160	0.75	0.66	0.24	0.06
R/2	100 lb. (*Wc*)	4	160	0.75	0.78	0.22	0.05

The experiments summarized in Table II were carried out on a much larger scale, in pots of a capacity of either 50 or 100 pounds. In the experiments in question the melting process was carried on for a period of 20 to 22 hours at a temperature measured on the glass-pot level, (that is, the interior temperature of the pot) of 1400°C. Increasing amounts of arsenic were added up to 10 pounds or 160 ounces per 1000 pounds of sand. The table records the amount of arsenic added to the batch, the approximate percentage which would be present in the glass if all the arsenic were retained, the actual amount of arsenic retained, and the percentage of alumina and iron oxide respectively in the glass.

Before attempting to draw a conclusion from these results it is desirable to point out that the arsenic content is not the only variable factor. The temperature of melting and the period of reaction are constant, but two different makes and sizes of pot were used, the makes being designated as *W* and *M*, respectively, the clay used being different.

Moreover, the extensiveness of attack depends to some extent on the order of melting in any particular pot; that is to say, a new pot usually suffers somewhat greater loss than one in which glass has previously been melted. As it remains in the furnace it normally acquires greater resisting powers. This would not, from the table, appear to be invariably the case; but again it may be pointed out for any particular addition of arsenic, the order of melting in most cases was for different pots, the several pots used here being noted as *Wa*, *Wb*, etc. For several concentrations of arsenic, however, meltings were done in the same type and size of pot so that four of the factors remain constant. Remembering this fact, it does seem quite clear that increasing the arsenic content of the batch tenfold makes no apparent difference to the extensiveness of corrosion as measured by the alumina and iron oxide content of the glass.

TABLE III

(*a*) MELTING IN CLOSED POTS OF 100 LBS. CAPACITY

Glass no.	Melting temp.	As_2O_3 in batch per 1000 lbs. sand (ounces)	Time in pot after last charge	Pot size and type	Calcd. As_2O_3% in the glass	Order of melt	Observed As_2O_3% in the glass	Al_2O_3%	Fe_2O_3%
527 P/4	1400	32	43	100 *W*(*a*)	0.15	1	0.12	0.39	0.04
5	1450	32	46	100 *M*(*a*)	0.15	1	0.11	0.60	0.06
6	1500	32	46	100 *M*(*b*)	0.15	1	0.11	0.50	0.05
527 O/4	1400	80	42	100 *W*(*a*)	0.37	2	0.29	0.47	0.04
5	1450	80	42	100 *M*(*a*)	0.37	2	0.30	0.74	0.06
6	1500	80	45	100 *M*(*b*)	0.37	2	0.28	0.94	0.09
527 R/3	1400	160	44	100 *M*(*c*)	0.75	4	0.66	0.43	0.06
4	1400	160	45	100 *M*(*c*)	0.75	1	0.66	0.69	0.09
7	1450	160	45	100 *M*	0.75	1	0.61	0.88	0.09
(*b*) MELTING IN OPEN POTS OF 50 LBS. CAPACITY									
527 P/7	1400	32	22	50 *W*(*a*)	0.15	1	0.13	0.57	0.07
9	1450	32	21	50 *W*(*b*)	0.15	1	0.14	0.49	0.06
10	1500	32	21	50 *W*(*b*)	0.15	3	0.15	0.86	0.07
527 O/7	1400	80	22	50 *W*(*a*)	0.37	2	0.28	1.24	0.10
8	1450	80	22	50 *W*(*a*)	0.37	3	0.31	1.46	0.10
9	1500	80	21	50 *W*(*b*)	0.37	2	0.30	0.64	0.09
527 R/5	1400	160	44	50 *W*(*c*)	0.75	1	0.59	0.64	0.09
6	1400	160	45	50 *W*(*c*)	0.75	2	0.59	0.53	0.09
9	1450	160	45	50 *W*(*d*)	0.75	1	0.54	1.29	0.13
10	1450	160	45	50 *W*(*d*)	0.75	2	0.51	1.46	0.12
13	1500	160	45	50 *M*(*a*)	0.75	2	0.41	6.37	0.55

This conclusion seems to be true for a melting temperature of 1400°. The question remains as to whether or not the arsenic compounds might show evidence of corrosiveness with the rise of temperature above this value, which is not frequently much exceeded in practice. A further set of data, abstracted from our researches and collected in Table III appears to indicate that they do.

In the first group, namely, those in 100-pound closed pots, the meltings were done in pots of the same type except in two cases at 1400°, about which we need not make comment since conclusions can be drawn from Table II in respect to this temperature. In this group also, it may be noted that the glass was in contact with the pot for approximately twice the length of time used in the meltings referred to in Table II; that is, the period was 42–46 hours subsequent to the addition of the last charge.

Comparing the results at 1450°, it would appear that there is a definite increase in the amount of Al_2O_3 and Fe_2O_3 dissolved as the proportion of arsenious oxide added to the batch was increased. The two available results for 1500° also exhibit this same increase.

The open pots were also of the same type except in one case, namely, that used for melting glass 527 R/13, but strict comparison must be confined to the glasses of the P and O series only, since these were in contact with the pot after the last charge for a period of 21–22 hours, whereas the R glasses of Table III (*b*) stood for 45–46 hours. With this difference in mind the results at 1450° indicate a considerably greater attack with the higher than with the lower arsenic concentrations, although the increase is not parallel with arsenic addition. The comparatively high percentage of alumina in glass 527 O/7 melted at 1400° must be regarded as accidental. At 1500°, the results are irregular. But although it would be unwise to make definite assertions of the corrosiveness of arsenic based on this second group of results, it would appear when all the results in Table III are considered, that at higher temperatures than 1400°, arsenic begins to have a somewhat increasingly greater corrosiveness toward fire clay, the attack increasing with concentration.

In forming a final judgment on the effect of arsenic in practice, we must consider the circumstances in which common soda-lime-silica glass is melted industrially. In normally efficient tank furnaces the maximum temperature of the glass will seldom exceed 1400°–1425°, and is often lower than 1400°, while the amount of arsenious oxide employed is not usually in excess of 2–3 lbs. per 1000 lbs. of sand in the batch, equivalent to 0.15–0.23% of arsenious oxide in the glass, assuming it all to be retained.

Now it is clear from the data set out in Tables I and II that even when an amount of arsenious oxide 4–5 times that used in practice is employed, there is no marked corrosion of fire clay at 1400°; at any rate, no corrosion that can be shown by increase in the amount of alumina and iron oxide taken into solution in the glass. Even at higher temperatures than 1400°, that is, at 1450° and 1500°, it is only when the amount of arsenic is in excess of that used in the industry that corrosion due to the use of arsenic can be traced. The final conclusion, therefore, to which I think we must come, is that under the conditions usually observed in practice in the melting of soda-lime-silica glass, any corrosive action due to the arsenic must be regarded as "not proven."

As suggested in the introduction to this paper, the observations recorded by McSwiney may bear an alternative explanation. The action of the arsenic may be indirect. The allegation (not favored by McSwiney) that selenium causes the corrosion of tank blocks is most probably to be associated with the increased transparency to heat rays which colorless glass has over green or other colored glass. Thus tank furnaces with 36 inches of green glass may be sufficiently deep to preserve the bottom blocks from the necessity of replacement for a considerable period; whereas for melting colorless glass, 42 inches depth had to be adopted, while more recently, 48 inches depth is frequently employed in bottle glass tanks. These practical considerations are evidence of an average higher temperature throughout the colorless glass in a tank as compared with green glass and the consequence must be a greater rate of corrosion due to higher temperature. But arsenious oxide is quite definitely a decolorizing agent for glass independently of selenium and therefore renders the glass more transparent to heat radiation. It is very possibly along these lines that the facts related by McSwiney are to be explained. It would be useful in this connection if comparative measurements were available of the temperatures at different depths in tank furnaces containing colorless glass and green glass, respectively.

The one object of this paper was to examine the possible corrosive action of arsenic compounds on fire clay refractory material. There is other information which may be deduced from the data recorded above in regard to the behavior of arsenious oxide in the melting of glass, but this subject will be discussed in detail in other papers.

DEPARTMENT OF GLASS TECHNOLOGY,
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Discussion

BY D. J. MCSWINEY[1]

It is a well known fact that the life of glass tanks may vary widely when different colored glasses are melted in them, even though the tanks are of the same design and operation, and constructed of the same refractory material; and the glasses not differing in composition, except for the relatively very small amounts of coloring and auxiliary materials used in the batches to produce the different colors.

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[1] Received May 6, 1926.

There are so many factors controlling the life of glass tanks that the importance of any one factor can be determined only when the effect of the other factors does not vary. This can be done in the case of tanks melting flint, amber, and light green glasses in the same plant, when the average life of a number of tanks melting glass of each color is considered, and when the base glass, the routine of construction and operation, the refractory material used, the temperature and pull carried, etc., are all essentially the same.

If we disregard those tanks in which an abnormally short life is evidence of an abnormal or poor operation or of poor refractory, the average life of selenium and arsenic decolorized flint tanks, melting a glass of the average bottle glass composition, under good operation at a temperature of 2450–2550°F, an average pull of about twelve square feet, and using the common level throat construction, is about eleven months; that of light green glass tanks under the same conditions is about fourteen months, and that of amber tanks about twenty-four months. The range of tank life under these conditions is from about eight to thirteen months in the case of flint tanks, ten to twenty-four months with light green tanks, and fifteen to thirty-six months in the case of amber tanks.

The life of the tank is here considered as the length of time between the filling of the first batch and the time when the glass breaks through the refractory wall. The average lives given above are not merely characteristic of the tanks of any one particular company but are approximately correct for all plants melting these glasses under the same conditions.

The majority of flint tanks with level throats go out through the throats, while most of the remainder go out through the side wall, usually at the metal line, a few through dog-house corrosion and occasionally one through the bottom. The majority of light green tanks go out through the side wall, and most of the remainder through the throat. Most amber tanks operated under the same conditions do not go out through glass attack, but usually through some derangement of furnace operation, such as clogged checkers, burnt out ports, etc., so that the average life of amber tanks, as far as glass attack is concerned, is greater than the twenty-four months given above.

The reason to which is usually ascribed the longer life of amber and green tanks over those of flint worked under the same conditions is a lower transparency of the first two glasses causing less radiant heat to penetrate to the bottom of the tank. However, while the bottom of an amber tank may be very much lower in temperature than that of a flint tank of the same depth and operated at the same surface temperature, it should not be assumed that the same ratio of temperatures holds true for the glass in the throats of the two tanks. Tanks are worked about 85% of their life and it is the glass which flows through the throat which causes corrosion, and in the majority of cases, flint tanks eventually collapse at this point.

The glass flowing through the throat of any tank is always much hotter than the glass at any other point on the same horizontal level throughout the tank, owing to the fact that a large portion of the glass which flows through the throat comes from the glass surface almost directly above the throat opening. Examination of the lines of flow of glass in tanks of different colors shows that a greater portion of the glass entering the throat comes directly from the surface in the case of colored glass than with flint. This, however, may be largely offset by a greater temperature drop in the case of the dark glass as it falls to the throat as a result of greater radiating power. It is the hot glass coming direct from the surface which causes throat collapse rather than the colder glass which works in from the lower levels, as is evidenced by the fact that throat corrosion always takes a mushroom or inverted pear shape.

While the lower transparency of the dark glasses may account for the decreased corrosion of the throats of amber and green tanks relative to flint, it is difficult to see how this can explain the decreased corrosion of amber and green tanks along the metal line, as variations in radiant heat transmission of the glasses should have little or no effect at this point. The life of the refractory along the metal line is usually in nearly the same ratio as the life of the tank. As stated above, many flint tanks go out at this point before corrosion of the throat is completed, and, in fact, many go out at this point in only eight or nine months. It is very seldom the case that a flint tank which has been operated for twelve or thirteen months will not be worn very thin at points along the glass line, but amber tanks are often to be seen which have been in operation under the same conditions more than twenty-four months and which will have a minimum thickness of more than $3\frac{1}{2}$ inches along the glass line.

The shortening of tank life resulting from the addition of arsenious oxide to green glasses to lighten the color is not susceptible to the same analysis as that of other colored glasses, owing to the fact that this practice is not common. However, I believe that the decreased tank life resulting in these cases is too pronounced and too regular to be merely a coincidence.

The difficulty of considering, without actual temperature measurements, the effect of color of the cold glass on the radiant heat conductivity of the glass at melting temperatures, lies in the fact that we do not know what may be the ratio of this conductivity of the same colored glass at low and at high temperatures. We know that the addition of arsenious oxide decreases the color of the cold glass, but not knowing the mechanism of the action of the arsenious oxide on the iron color we cannot judge if this increased light conductivity holds at high temperatures.

The light green glass, the life of melting tanks against which is stated above, contains only about .06 to .10% iron oxide. The larger part of the iron is usually maintained in the ferrous condition through melting under reducing conditions, or a small amount of cobalt oxide is added to give the glass a bluish cast. The amount of coloring material in these light green glasses may then be less than that in many flint bottle glasses which may contain as much as .07% iron oxide and sufficient color (from the decolorizer) to complement the iron color. Moreover, the amount of iron oxide in different flint soda-lime glasses varies from .02 to .07% and the arsenic oxide used does not vary in the same ratio. The variation in transparency of these flint glasses when cold, due to the variations in their iron contents and the proportionate amounts of decolorizer used, does not appear to affect the life of tanks, but the variation in the amount of arsenic used does appear to decrease tank life out of proportion to the apparent effect of the arsenic addition on the color of the cold glass.

When the color of the cold glass is dependent on the presence of colloidal particles, as is the case with selenium, sulphur, and similar colored glasses, it seems probable that the transparency of the glass at high temperatures compared to that of a glass colored with cobalt or iron or similar coloring materials, may be much greater in proportion to the transparency of the two glasses when cold, because a large part of the colloidal coloring is apparently developed while the glass is cooling from the melting temperature. For example, a sulphur amber, when rapidly chilled will usually not show nearly the depth of color that is shown by the same glass when chilled at the normal rate. If this is generally the case with amber glass melted in tanks, it is still more difficult to see how differences in radiant heat transmission can cause such a difference in the rate of corrosion along the metal line as actually obtains in flint and amber tanks.

It is well known that when amber and flint glasses of the same composition are worked by hand the working of the amber glass is much more difficult than that of the flint, being more difficult to gather and setting much more rapidly. While in the case of hand working the increased setting rate of the amber glass may be partly or wholly ascribed to more rapid cooling consequent to greater radiating power, it is not easy to see how this can fully explain the fact that in the rapid forming Owens machine, when worked at full capacity, an amber glass requires a higher working temperature than a flint of the same composition to get the same results.

When sufficient circulation obtains in a pot melt to so mix the glass that the products of solution of the refractory walls are thoroughly spread throughout the melt, the increase in the alumina or iron content of the glass as a result of the refractory solution can be considered a measure of the degree of solution of the refractory. However, the solvent power of the glass for clay refractory is not the only factor determining the life of a refractory container against glass; the factor which ordinarily determines this life is not the rate of solution of the refractory but rather the penetration of the refractory walls by the glass. The commercial pot which is worn down uniformly through use to a thin shell is the exception rather than the rule, the average life of glass pots and tanks being directly determined by local penetration. The factors which influence refractory solution and penetration are not the same or do not have the same values in the case of tank blocks as in that of pots, and consequently even when the same refractory is used in the two containers, the life in each case cannot be compared with that in the other.

Aside from the penetration resulting from a local condition or defect of the refractory, or a localized high temperature, the penetration of the refractory is determined by the character of the glass. The property of the glass which primarily determines the degree of penetration is not the solvent power of the glass for the refractory material but rather the fluidity of the glass and its viscosity-temperature relations.

In general, with pure combinations of soda, silica, and lime, the solvent power of the glass for silica and alumina tends to vary as the fluidity, but it does not appear at all impossible that the additions of small amounts of materials such as the carbon and sulphur used in amber, and the arsenic in flint may have an influence on the penetrative power of glasses, by influencing the viscosity-temperature relations of the glass either by affecting the degree of molecular association of some of the glass constituents or the rate at which the glass acquires a stable "nature," in much the same manner as the addition of small amounts of some materials can affect the viscosity and rate of maturing of gelatin, silicic acid, and similar hydrosols.

In flat glasses in which selenium is used as a decolorizer and the iron content of which does not exceed those of some flint bottle glasses, arsenic is not ordinarily used. Tanks melting these glasses often have a life exceeding twenty months, and while these tanks are not constructed with throats, the life of the refractory along the glass line is very much higher in these tanks than it is in bottle tanks, although the average operating temperature of these flat glass tanks is higher than that of bottle tanks, and although salt cake, which apparently increases the solvent power of glass for refractory, is used in these glasses to lessen scum formation. The setting rate of these glasses is, of course, very much higher than that of bottle glasses. In this respect, it may be well to point out that the glass on which the results given in Dr. Turner's paper were obtained has a higher setting rate than practically all the soda-lime-selenium and arsenic decolorized flint glass made in this country.

As the arsenic exists in the glass combined, probably with alkali, its addition above a nominal amount tends to change the nature of the base glass in that it lessens the amount of soda available for the silica. As the glass contains near the limit of silica which under ordinary working conditions can be readily assimilated, the action of the increased content of arsenic oxide in decreasing the available soda to silica ratio, even assuming, as to me appears probable, that the arsenic is present as the meta-salt, and disregarding any possible solvent action of the arsenate, would itself tend to decrease the solvent action of the base glass on the silica of the refractory by increasing the silica and decreasing the soda content of the base glass; this may possibly account for the observed decrease in refractory solution with increase in arsenious oxide at the lower temperatures.

A NON-ACTINIC COBALT-BLUE GLASS[1]

By W. W. Coblentz and A. N. Finn

ABSTRACT

A non-actinic blue glass is described. The substitution of cerium oxide for a part lime and the addition of a small amount of cobalt oxide in an ordinary soda-lime glass produces a glass which, in 5 mm. thickness, absorbs practically all the ultra-violet rays. The composition of the glass, its ultra-violet absorption, and the visible spectral transmission are given.

Colored glasses have been used for years to protect the eyes when looking at bright lights or into furnaces, but in some cases these glasses do not give the proper protection. Although they do reduce the intensity of the transmitted light, some of them do not entirely absorb or "cut out" the harmful ultra-violet rays.

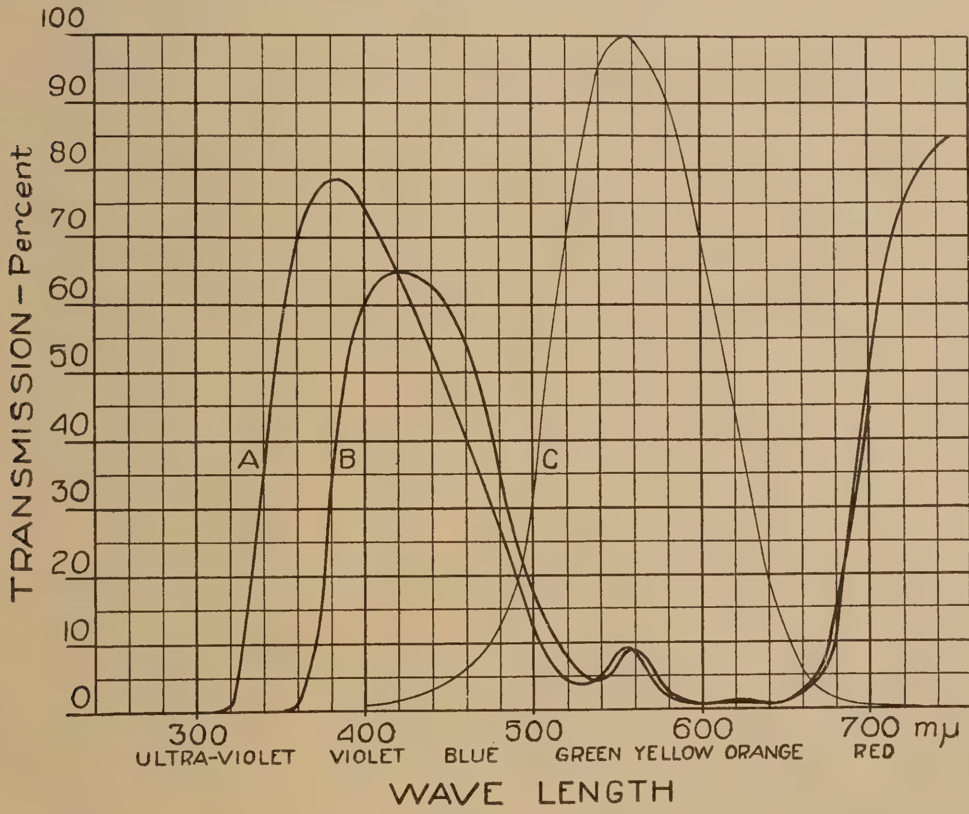

Fig. 1.—Spectral transmission of A, an ordinary cobalt-blue glass, 2.11 mm. thick; B, the cobalt-cerium glass (No. III), 2.85 mm. thick; C, relative visibility curve.

Safety engineers have insisted that men working around open-hearth or other high-temperature furnaces use a colored glass which reduces the intensity of the light from the furnace and also offers good protection against the harmful ultra-violet rays. However, most furnace operators themselves prefer a cobalt-blue glass regardless of the fact that it only gives partial protection against the harmful ultra-violet rays, maintaining that they can observe furnace conditions better through a blue than through other colored glasses. This prejudice is probably due to their greater experience with a blue glass, because other colored glasses are now being used with satisfactory results in some industries.

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[1] Published by permission of the Director of the National Bureau of Standards of the United States Department of Commerce. Presented at the Annual Meeting. American Ceramic Society, Atlanta, Ga., Feb., 1926 (Glass Division).

The ordinary cobalt-blue glass does not absorb the ultra-violet rays which are harmful to the eyes (those beyond 0.310μ)[1] much, if any, more than ordinary colorless glass. Glass containing cerium oxide transmits practically all the visible spectrum and absorbs the harmful ultra-violet rays.

If cobalt and cerium oxides could be introduced into the same glass without losing their characteristic effects, the desire of furnace operators for a blue glass would be gratified and, at the same time, the requirements of the safety engineers for a non-actinic glass would be met.

In order to determine if such a glass could be made, three experimental glasses of the same general compositions were melted at the Bureau of Standards. The composition of each of these glasses (computed from the batch composition) is as follows:

	I	II	III
	Per cent	Per cent	Per cent
SiO_2	69.6	69.5	69.5
CaO	6.0	12.8	6.0
CeO_2	6.8	0.0	6.8
CoO	0.0	0.1	0.1
Na_2O	17.6	17.6	17.6
	100.0	100.0	100.0

The glass melted and fined readily at 1425°C and it worked easily. The apparent color of the glass was so similar to that of the simple cobalt glass that it was practically impossible to differentiate between them by visual inspection.

The ultra-violet transmission of the three glasses is given in the following table:

TABLE I

Transmission in Per Cent

Glass no.	Thickness	Ultra-violet spectrum*					
	mm.	0.280μ	0.302μ	0.313μ	0.334μ	0.365μ	0.405μ
III	2.90	0.0	1.4	13.4	64.9	87.0	84.2
I	2.02	0.0	0.0	0.0	0.0	3.7	68.9
III	2.80	0.0	0.0	0.0	0.0	2.5	62.9
III	5.00	0.0	0.0	0.0	0.0	0.0	41.5

* 0.380μ is commonly considered as a short wave length limit of the visible spectrum.

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[1] J. H. Clark, Lighting and Its Relation to Public Health, Williams and Wilkins.

The spectral transmission[1] of an ordinary cobalt-blue glass[2] and the cerium-cobalt-blue glass is shown in Fig. 1.

From these data it is evident that cobalt and cerium oxides can be combined in the same glass without losing their characteristic effects, and that a cobalt-blue glass of the kind described above will afford greater protection against the harmful ultra-violet rays than the ordinary cobalt-blue glass.

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[1] Measurements made in the Colorimetry Section, Optics Division, Bureau of Standards.

[2] Gibson and McNicholas, Bur. Stand., *Tech. Paper*, No. 119 (Fig. 17, curve *D*).

STANDARDIZED PROPORTION OF THE GREEK VASE AND ORNAMENT[1]

By Robert W. Gardner

ABSTRACT

This paper demonstrates that in Greek art geometry and not inspiration was the basis of proportion and the fundamental of design. It gives the actual method, hitherto lost, that was employed in the application of geometry to design by artists and craftsmen of the fifth century B.C. The subject matter contained in this article was obtained by its writer in an investigation into the proportions of the Parthenon. In his book[2] "The Parthenon: Its Science of Forms," the writer deals only with the temple and the design of the Acropolis and of the city of Athens and its port of the Piraeus, but in this article he gives in a simplified form the canon of proportion which can be applied today in every branch of art, the canon which the Greeks employed in producing the masterpieces of the Golden Age of Pericles.

The purpose of this paper is to demonstrate that the basic element of all Greek design of the classical period is geometric; that the Greeks used a standardized scale of proportions which applied in all their variation of design; that this scale was one of commensurable areas, geometrically obtained and starting from a nucleus or center and expanding outwardly; that the method of application was direct, simple, and uniform; and that in it no arithmetical calculations were used, but the square and compasses alone. Originally the method was taken directly and in its entirety from Egypt of the Fifth Dynasty. As developed by the Greeks it applied to pottery, architecture, sculpture, and allied arts, as well as to the musical scale of Pythagoras. The geometry involved is so simple that anyone who understands the elements of geometry can grasp and apply the analysis.

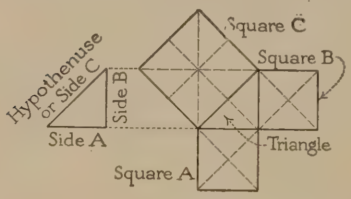

FIG. 1.—Right angle triangle.

FIG. 2.—"The square on the hypothenuse of a right angle triangle equals the sum of the squares on the other two sides." By counting the equal constituent triangles in *A*, *B*, and *C*, it is self-evident that area of $A+B$=area of *C*.

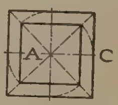

FIG. 3.—By drawing square *A* on triangle, Fig. 1, and by rotating the hypothenuse or diagonal to the axes of symmetry, square *C* of Fig. 2 appears concentrically placed on *A* and double the area of *A* (ratio 1:2).

We have in America all of the elements save one of a successful and dominating industry: the materials, the skill in handling, the capital, and enthusiasm; but have we the art, the science of designing the shapes, the forms, the decorations of these shapes, so that two thousand years from now these objects we make will be treasured as priceless heritages, as the pottery and statuary and architecture of Greece is treasured today? In a recent convention, it was admitted that we have not.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926 (Special Session). Received March 24, 1926.

[2] "The Parthenon: Its Science of Forms," by Robert W. Gardner, published by the New York University Press.

Americans Lack Proportioning

If it is admitted that our designs are imperfect, even when they are the products of our best talent, then we must either admit a general personal inferiority, or the lack of some instrument by which the Greeks in their customary objects attained their matchless results. It is the writer's opinion after delving into this subject for several years, that the answer is in our lack of method in proportioning. We copy blindly the beauty of another age whose science of design was lost two thousand years ago and comfort ourselves with the thought that art perhaps is inspirational, endowed by nature, and grows from an innate feeling of inspired personality. This leaves us at the mercy of the archaeologist instead of throwing us on our own resources. We are all familiar with the results.

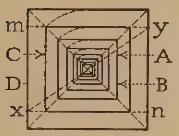
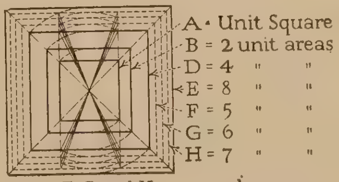


FIG. 4.—The process of Fig. 3 is repeated outwardly and inwardly to produce a geometric series of commensurable squares in binary ratio (1:2:4:8:16). These may be called primary squares.

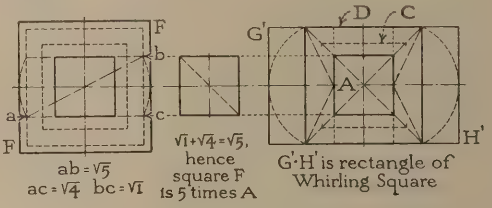
Underlying the design of the simplest object, as well as the most grandiose scheme in Greek art, there is the basic geometrical science that determined inexorably the proportions used. That personality, as we commonly know it, was subordinated to law and order, but by obtaining continuity and unity of design they really expressed the highest form of personality with all its feelings and strivings. This canon of proportion, this law of design helped, not hindered, the rational mind that won freedom by hard obedience to law. To the Greek mind all particulars were parts of a united whole and this philosophy was expressed in his art whose beauties reflected logic, simplicity, and order. His method we can apply today in shaping our commonest necessities of life, from the household utensil to the skyscraper.



F, G and H are secondary squares.

FIG. 5.—By prolonging opposite sides of any unit square as *A*, to the sides of another square in the series as *D*, rectangles are obtained whose diagonals form sides or roots of other commensurate square. Thus *D* being 4 times *A* it follows that *F* in area is 5 times the unit *A* for the reason that 4+1=5. See Fig. 6.

Hambidge Dynamic Symmetry It was the late Jay Hambidge who first aroused a complacent world to the fact that geometry was the basic element of design and in his book, "Dynamic Symmetry," furnished abundant proof to sustain his contention. Unfortunately he furnished no consistent way of applying any method to a design. Rather, the individual was left to experiment for himself in his own designs.



FIGS. 6 AND 7.

In the following demonstration I wish to stress particularly that the underlying principle of design is the unfolding or outward growth from a single unit: a square placed at the crossing of two axes of symmetry and determining all quantities or dimensions from squares increasing in geometrical ratio in even multiples in area of the original unit. This is the method of growth in nature, in all organic life where all organisms are built up by accretion from a nucleus. The Greek designer was following a natural law.

We must first analyze the simple principles of Euclid involved in the method. As far as the vase and sculpture are concerned, one sheet of details will explain the whole thing. If time permitted, the variations of the geometrical method to apply to the temple and city planning could be given. Fundamentally, however, they are all the same. They differ in the ratio of increase: the unit is doubled in one, tripled in another, and in the Parthenon and Doric temples generally the increase is pentamerous, or in multiples of five.

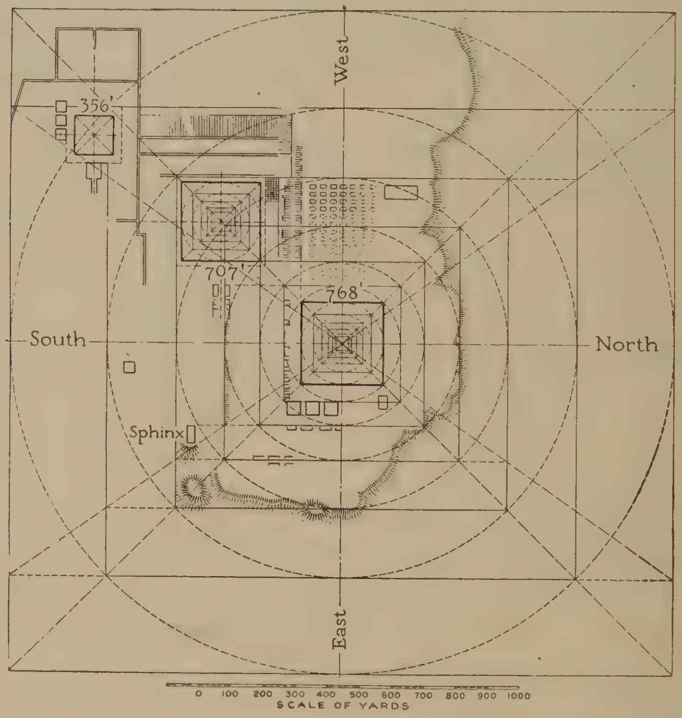


FIG. 7A.—The pyramids of Gizeh, B. C. 2850. (From plan by Lepsius.) The survey shows that not only the main objects but the subordinate pyramids, tombs, and temples were laid out in rigid accordance with the scheme of commensurate squares. Possibly to get the rock fill for the structures they cut back the plateau. In cutting as in filling they conformed to the geometric scheme.

In the Erectheum there is a combination of the doubling, or octave ratio, with the tripling ratio, which exactly duplicates the frequency ratio of vibrations in the musical scale of Pythagoras as they apply to the minor and major thirds and sixes. This statement may be regarded as an announcement of a discovery within the last few months. Its significance will be apparent to our modern composers who are striving without scientific basis to arrange a new scale of musical intervals.

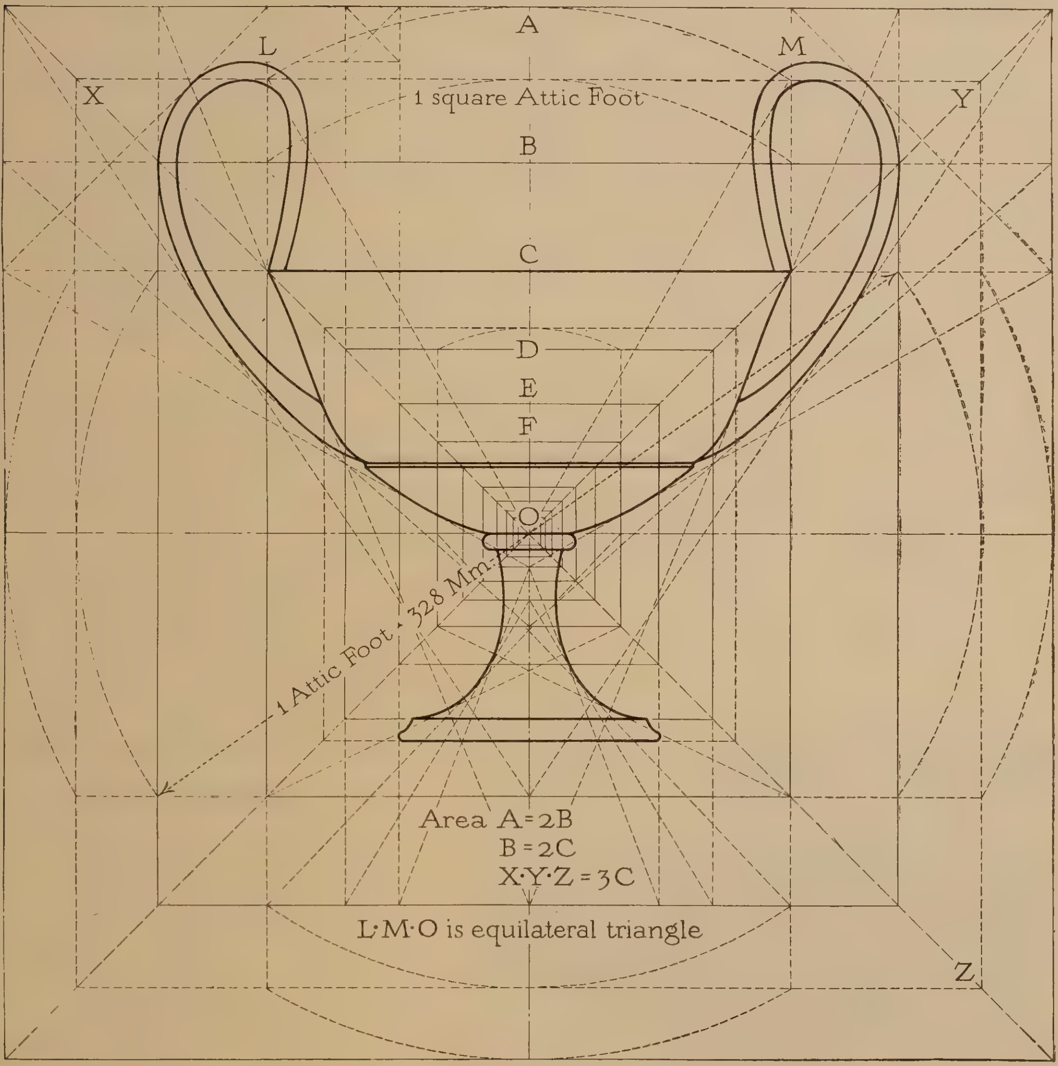


FIG. 8.—Kantharos in the Boston Museum of Fine Arts. The width of the brim is marked by square *C*. The width of the handles is marked by *B*. The height of the handles by square *XYZ* which is three times the area of square *C*. The base comes within a square five times the area of *F*. The smaller details are obvious.

I shall show carefully measured drawings with the application of the single geometric scale which standardizes and controls the series throughout. As designers, we are interested, not as archaeologists or historians, but as students looking for something that will help us to attain beauty and appropriateness of forms.

The first geometric form to consider is the right-angled triangle. (Fig. 1.) Pythagoras demonstrates that in such a triangle the square of the hypothenuse is equal to the sum of the squares on the other two sides. (Fig. 2.)

Figure 2 shows by means of the diagonals that the larger square is double the area of the two squares, as the triangles are all equal, four in each of the smaller squares and eight in the larger one.

If we keep this proposition in mind and proceed to draw a series of squares along a common axis, each square having for its sides the diagonal of the preceding square, we have a series in geometrical sequence each double the size of its predecessor in area. (Fig. 4.)

These squares are now arranged on two axes of symmetry. We have an orderly, convenient scale of proportionate parts arranged so that the relationship is present, but not apparent, unless we use the compass to test the diagonals.

Furthermore, from this series of squares in doubling ratios, all of the various geometric motives can be obtained; the rectangle of the golden section, the rectangle of the square root of five, or of three. (Figs. 5, 6, and 7.)

Aside from the simple or primary squares in doubling ratios, which may be likened to the octave in music, we can, by prolonging the sides of a small square outwardly to the perimeters of the larger squares and using the diagonals of the resultant rectangles as sides of harmonic squares, get all the intermediate square areas, all commensurable with the two squares used in the rectangle. Between 4 and 8 unit areas we can get 5-6-7 unit areas; that is, in the ratio of 4 to 5, 4 to 6, and so on.

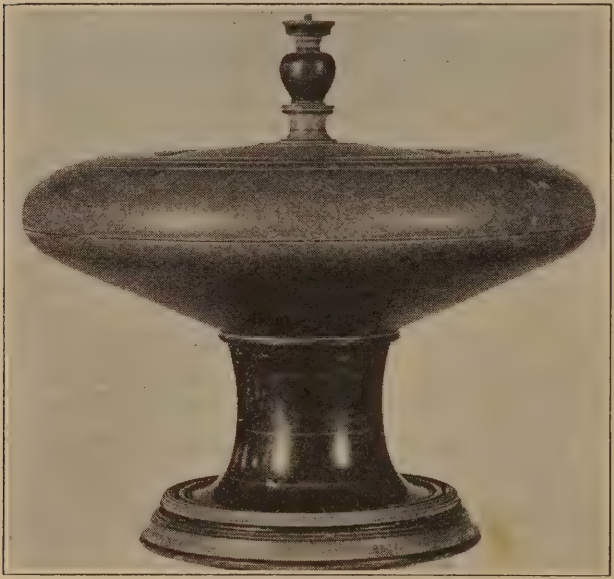


Fig. 9.

The next step is to standardize our series of squares by starting with a square that would run the series in units of a standard foot.

The Greeks, with their usual finesse, did not apply the measurement directly and obviously on the sides of a square, but on the diagonal of a rectangle whose sides were in the proportion of one to the square root of two. On the line oblique to the two axes of symmetry they proceeded to lay off their squares. See line *x–y*, Fig. 4, which should be one Attic foot if drawn full size. The rectangle *myxn* is a root 2 rectangle.

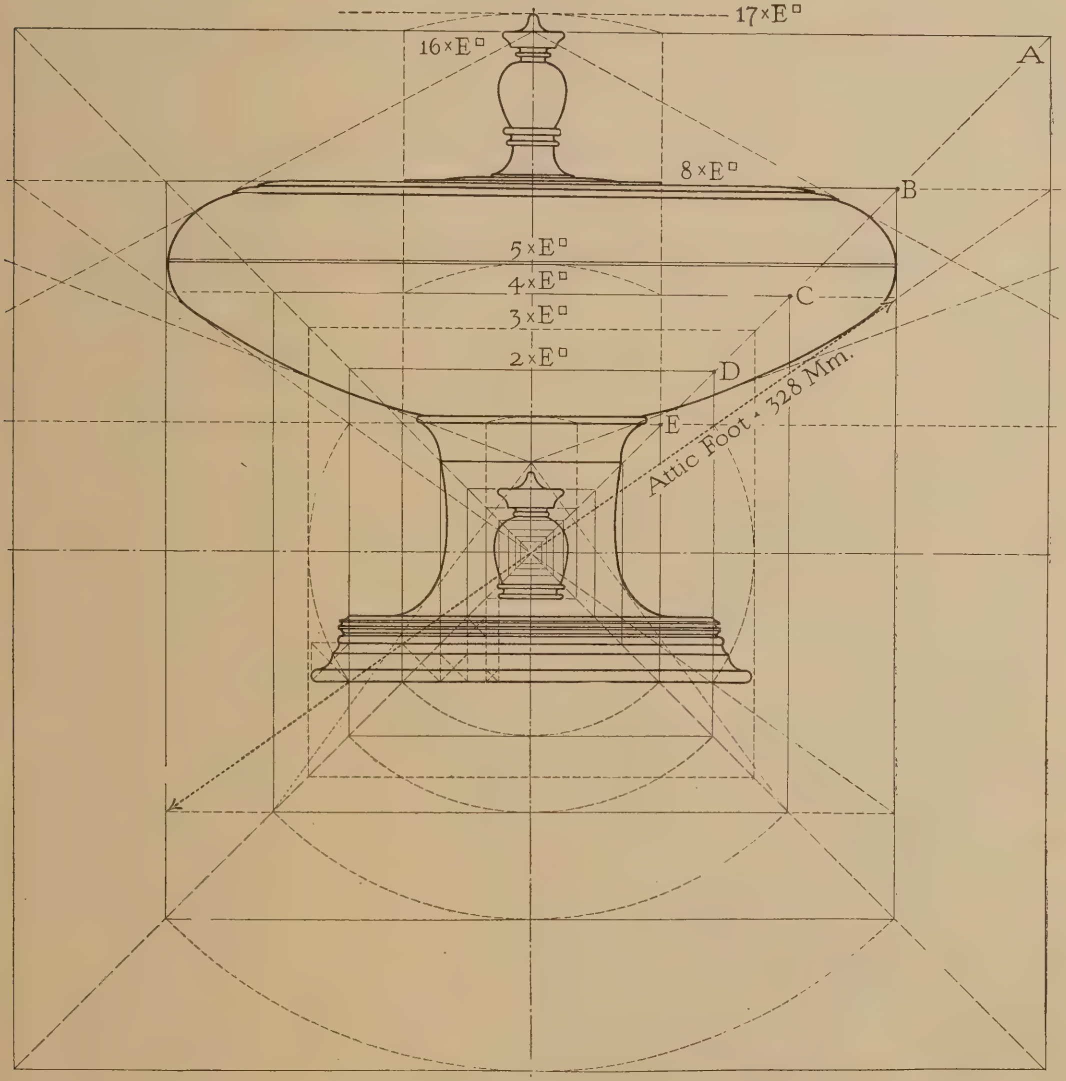


FIG. 9A.—Perfume vase from the Boston Museum. The dotted line marking the tip of the handle is the side of a square 17 times the area of square *E*. The incised line so marked is 5 times the area of *E* if the square were completed. The diameter of the foot is inscribed in a square 3 times the area of *E*. The other squares are obvious, and run in the geometric, binary series. They are identical in size with the squares similarly lettered in the other drawings. All are properties of the Attic foot.

We now have a series of squares whose sides, diagonals, differences, and sums are all related to each other and to a national system of measurement running from the infinitely small to the infinitely large area, or over any intermediate range that may be perfectly adapted to the technical requirement of our design. We have unity, continuity, relationship, and adaptation.

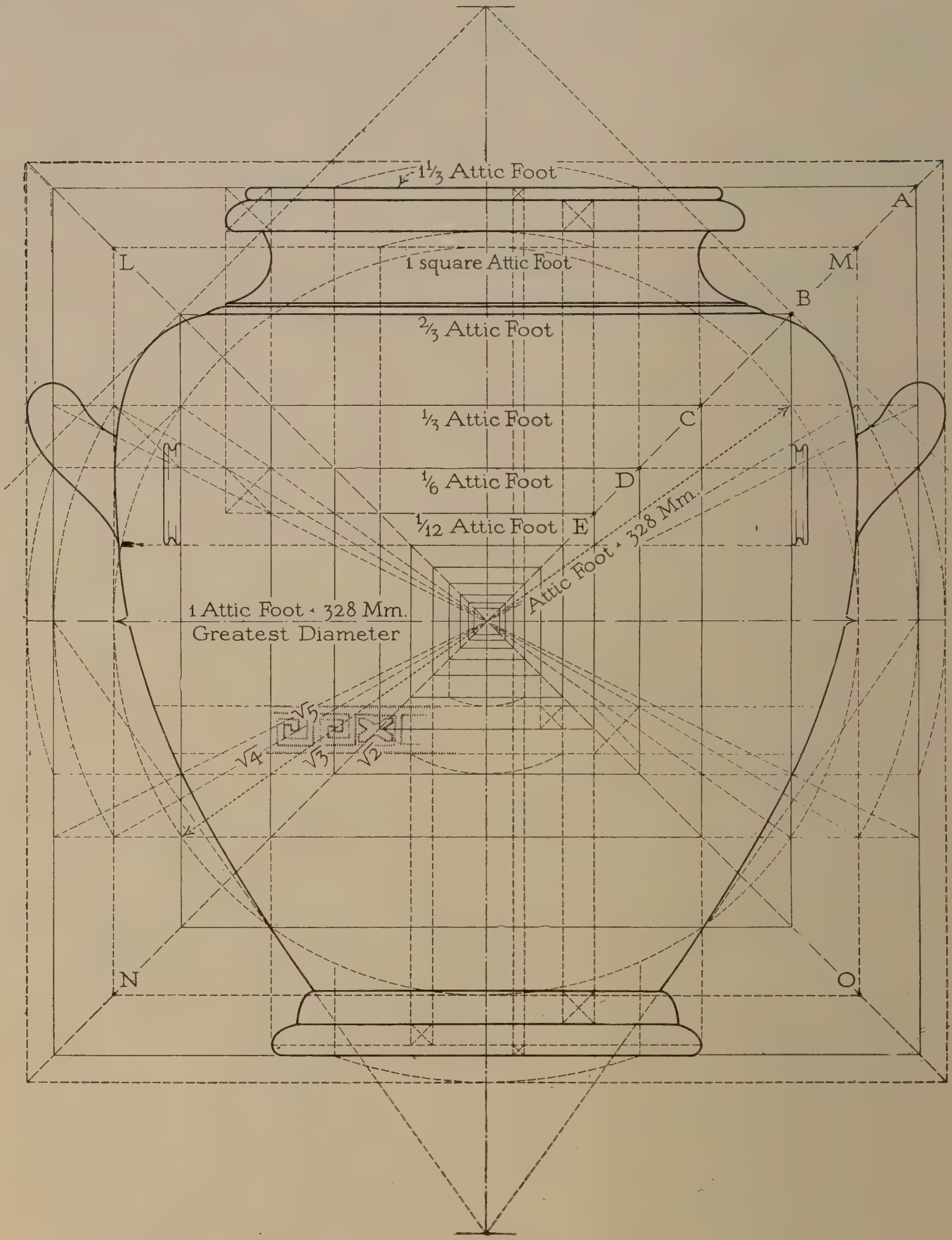


FIG. 10A.—Gage of Attic foot, 328 mm. Stamnos 00.342 Museum of Fine Arts, Boston. This stamnos seems to be the standard gage for the whole Attic system. The square *LMNO* is exactly one square Attic foot. It exactly inscribes the greatest diameter of the stamnos. The square *C* exactly inscribes the smallest diameter of the neck and is $\frac{1}{3}$ Attic foot. Square *B* is $\frac{2}{3}$ Attic foot or twice the area of *C*. Square *A* is 4 times the area of *C* or $1\frac{1}{3}$ Attic foot in area.

The great advantage in this scale, which will be at once apparent to the designer, is that any given object can be so laid out in plan that all its parts will be related to each other, and these in turn can be related to the room, to the building, and to any general scheme, and finally would be related in common with a standard unit of measurement.

All of this is accomplished with a minimum of effort as far as proportions are concerned, but with absolute freedom in combining the elements and in applying them as sense of fitness directs. It was with this instrument that the Greek artist standardized his proportion.

The earliest application of this series of squares, as far as I know, was in the grouping of the three pyramids of Gizeh. (Fig. 7A.)

The details shown on the photographs are located on the map. I have checked up several frieze compositions and find that the system was general in its application. No attempt will be made to introduce any of the frieze designs at this time.

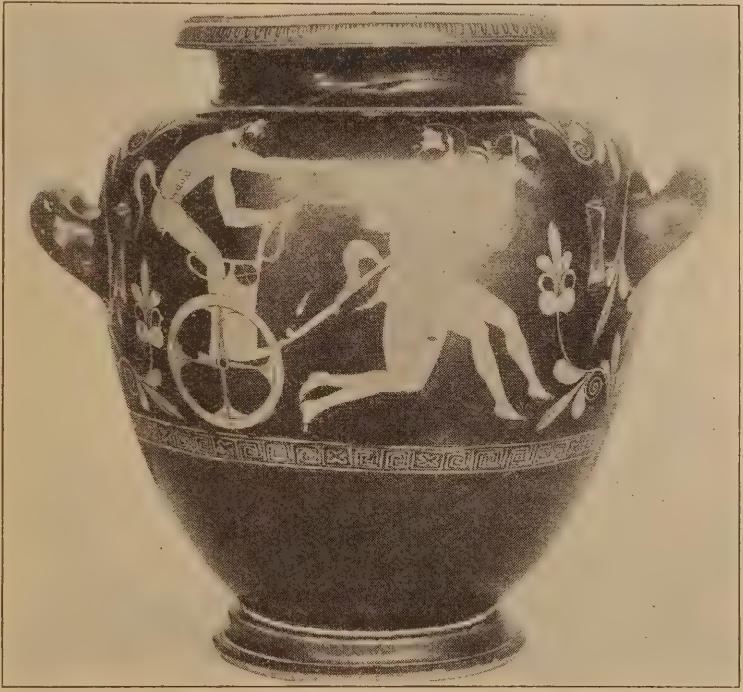


Fig. 10.

It is a historical fact that Thales, the Greek philosopher, visited Egypt in the 6th Century B.C. and carefully measured the pyramids. It is unlikely that any knowledge of the system of proportion existed in the world at that time. Egypt had been under the sway of the Ethiopian kings for two or three centuries and its civilization was at a low ebb. He evidently rediscovered the lost art and when he returned to Greece he brought with him and handed down his knowledge to a very small group of philosophers and their disciples and it was the heritage of Athenian scholars until in some way it was lost again—when, no one knows; certainly before Rome ruled over Athens.

I am indebted to L. D. Caskey's book giving the dimensions in meters of the objects in the Fine Arts Museum of Boston. One measured drawing, done carefully and conscientiously, is worth to the student

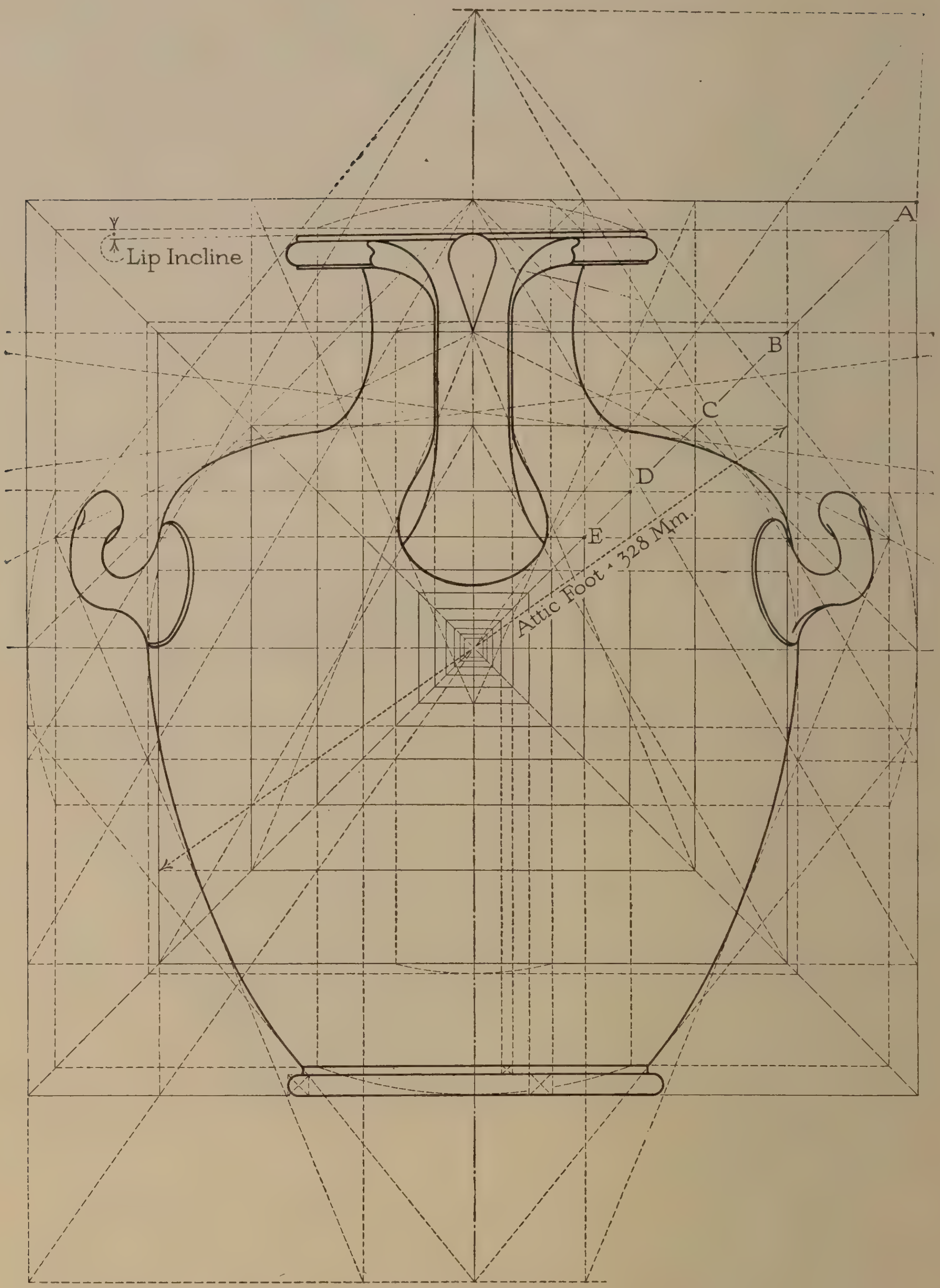


FIG. 11.—Bronze hydria. (Metropolitan Museum, New York.) The author has carefully measured this hydria. The lip is considerably "out of square" and the side lugs do not conform to any system of commensurable areas, as far as the writer can discover. The measurements and proportions are at variance with those given in Hambidge's book. The slight variations from rigid symmetry in accessories while adhering to it in the main body give an irresistable charm to this example and seem to put it in the class with the Parthenon itself.

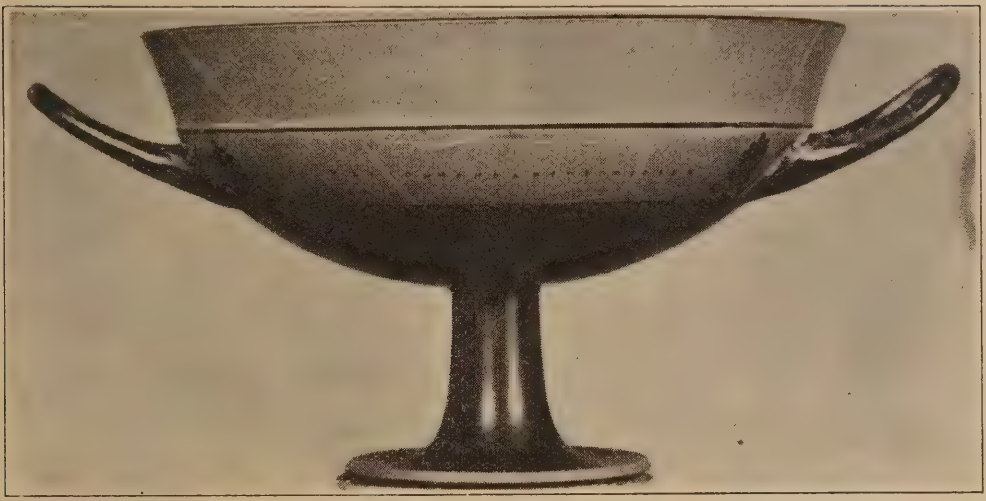


FIG. 12.

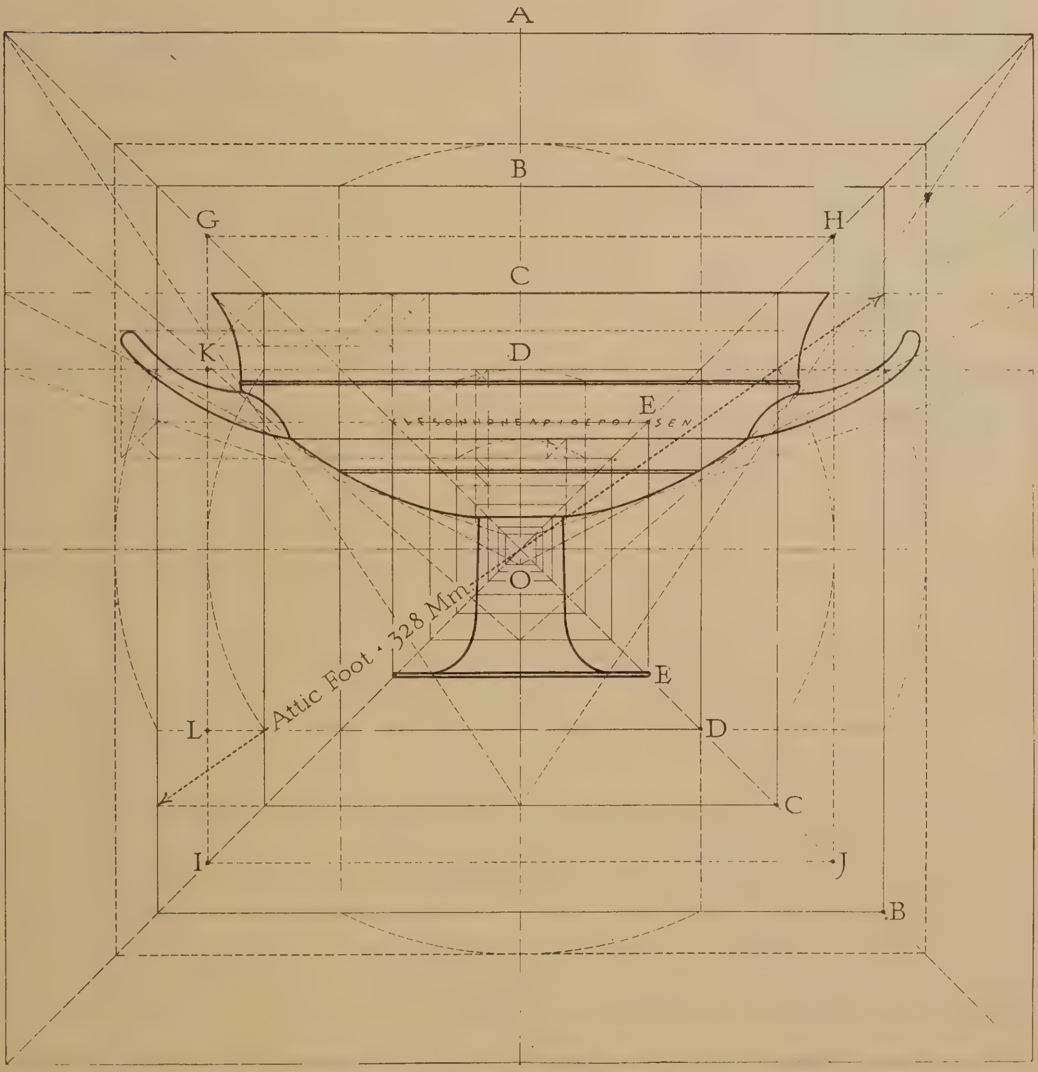


FIG. 12A—Kylix signed by Tleson, Museum of Fine Arts. *C* being $\frac{1}{3}$ Attic foot (see Fig. 10) then *D* being $\frac{1}{2}$ *C* is $\frac{1}{6}$ Attic foot. But *KLO* is an equilateral triangle, hence square *GHIJ* is 3 times the area of *D* or it is equal to $\frac{1}{2}$ Attic foot.

one hundred photographs. From the dimensions on his plates I was enabled to make my drawings full size for study and comparison.

My development of the system of vase design proceeded at the same time that the Parthenon study was in progress. Facts easily discernible in the vase pointed to analogies in the more obscure design of the temple, and reciprocally the temple design helped in the study of the vase. From the two the whole study unfolded. It is still in progress. When it will terminate or where, I cannot say. The preliminary studies of the temple of the Erectheum and of the temple of Apollo in Arcadia are well advanced, and of the latter temple there are illustrations of the application of the squares to the architectural members and the statuary.

The application of the standard scale to the Greek vase and architecture is shown in the various figures. (Note that the actual sizes of the squares are identical in the figures.)

To recapitulate: After a careful survey of the measurements of Penrose that apply to the Acropolis and the Parthenon at Athens, from those of Milchöffer applying to the city and port of Athens, from the map of the pyramids of Gizeh by Lepsius, and from the measured drawings of the Greek vase by Caskey, it is evident that in Hellenic art of the classic period, as well as in its most remote sources in a deeper antiquity, all dimensions in length, breadth, and thickness are determined and placed by a uniform series of commensurable squares progressing from a nucleus and expanding mechanically in geometrical progression on axes of symmetry that intersect on the nucleus.

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A METHOD FOR THE DETERMINATION OF THE RELATIVE SURFACE AREAS OF POWDERED MATERIALS[1]

By W. A. Koehler

ABSTRACT

The ratios of the surfaces of powders of different degrees of fineness are obtained by determining the relative amounts of a radioactive substance, ThB, adsorbed on the surfaces of the powders. The ThB is dissolved in an ammonical solution of water or alcohol, and equal-weight samples of the various powders are placed in equal volumes of this radioactive solution. After adsorption equilibrium is complete, 10 cc. of the clear supernatant liquid of each sample are evaporated to dryness on watch glasses, and the relative radioactivities of the deposits are measured in an electroscope. Since, for a given concentration of radio-active solution, the degree of adsorption is not a straight-line function of the surface exposed, an adsorption curve must be determined for each material studied.

Various methods have been proposed from time to time for obtaining some function that would express the degree of fineness of various powdered materials. This problem is of special interest to the ceramists, paint manufacturers, rubber workers, and to the various industries that use charcoal or other adsorbing materials. In most cases the results have been expressed as *average particle size.* But Perrott and Kinney[2] point out clearly that the term "average size" may have widely different interpretations, and must in each case be defined.

In the various methods proposed for measuring the size of particles, the error is usually of necessity great and indeterminate. In some cases a function of the surface is measured directly, or the particles are assumed to be spherical or of some other definite geometric figure and the diameters or other lineal dimensions are measured, and from this the volumes or surfaces are calculated. Paneth and Vorwerk[3] have shown that for lead sulphate the error is about 100%. For materials other than insoluble lead compounds the degree of error has not been determined. The determination of the *specific surface* of powdered materials is so far limited to those substances having radioactive isotropes.[4]

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[1] Contributed from the Chemical Engineering Laboratory, West Virginia University, and the Physical Chemistry Laboratory, University of Wisconsin. Received Jan. 15, 1925. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (General Science Session.)

[2] "The Meaning and Microscopic Measurement of Average Particle Size," *Jour. Amer. Ceram. Soc.*, **6,** 417–39(1923).

[3] "A Method for the Determination of the Surface of Adsorbing Powders," *Z. physik. Chem.*, **101,** 445–79(1922).

[4] Paneth and Vorwerk, *loc. cit*; Koehler and Mathews, *Jour. Amer. Chem. Soc.*, **46,** 1161–64 (1924).

Adsorption of Thorium B a Function of Surface

In the method presented in this paper, relative surface area measurements are made on the assumption that for a given material, presenting clean-cut surfaces, the adsorption of thorium B is a function of the surface, regardless of the degree of fineness of the material studied.[1] By determining with the aid of an electroscope the amount of thorium B adsorbed, the surface area relations are calculated.

Procedure Definite quantities of the material to be examined are placed in small Florence flasks or preferably straight walled centrifuge tubes of about 50 cc. capacity. To each sample are added 20 cc. of the radioactive solution, obtained as follows: A piece of platinum foil 3.5 sq. cm. on a side and attached to a platinum wire is placed inside a tube containing a mixture of barium bromide and radio thorium, the foil being so suspended as not to touch any of the material in the tube. The amount of thorium B collected can be increased by connecting the foil to the negative terminal of a 500-volt d.c. line. The foil is then immersed for 20 minutes in a solvent, consisting in most cases of either distilled water or of ethyl alcohol, with or without a few cc. of ammonium hydroxide solution. After removal of the foil, 20 cc. of the radioactive solution are pipetted into each of the tubes containing the samples. In addition, an empty tube is also given 20 cc. of the solution.

Each sample will adsorb a definite amount of the radioactive material from the solution, the amount adsorbed being a function of the surface exposed. In order to hasten equilibrium, a glass rod 3 x 120 mm. is placed in each tube, and the tubes are then placed in a shaking machine. The time necessary to bring about equilibrium must be determined for each kind of material studied; equilibrium was practically complete in all cases in thirty minutes. Table I and Fig. 1 show the progress of adsorption with increasing time.

The tubes with the samples and the radioactive solution are then centrifuged until all suspended matter is thrown down and only clear liquid remains above. Ten cubic centimeters of the liquid are pipetted from each tube and placed in brass cups or in watch glasses and evaporated to dryness on a water bath. When cool, the cups or glasses are placed in the lower chamber of a Lind alpha-ray electroscope and the

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[1] This still remains to be demonstrated, and may not be strictly true when comparing relatively granular with colloidal particles, but it is generally conceded by physical chemists that for a given material, the relative amount of adsorption is a function of the surface exposed. See any test on physical chemistry, as Getman, or Washburn, or Ostwald's Colloid Chemistry.

TABLE I

PROGRESS OF ADSORPTION WITH TIME

0.100 gm. quartz in each case, (100–150 mesh)

No.	Time of shaking, min.	Seconds required for leaf to pass over scale	No. of div./100 sec.	Natural leak, div./100 sec.	No. of div./100 sec. corrected	% Th B adsorbed
1	5	23.3	430	3	427	21.7
2	10	25.8	388	3	385	25.0
3	15	28.0	357	3	354	26.1
4	30	28.6	350	3	347	26.6
5	60	28.8	347	3	344	26.9
6	(blank)	10.8	928	3	925	0

activities of the deposits on each determined. These are expressed by the number of seconds required for the leaf to pass over the scale of 100 divisions (hereafter referred to as "seconds drop").

The electroscope was carefully prepared to give accurate readings. Instead of the customary gold leaf, an aluminum leaf was used. By using a carefully selected piece of foil from which to cut the leaf, and taking care not to fold or kink it in the mounting, it is possible to mount a leaf that will consistently pass over the scale with a steady motion.

The electroscope was charged by connecting its charging terminal to the negative terminal of a high voltage d.c. line. The voltage was obtained from a motor-generator set on which the voltage could be regulated by a rheostat over a range of 400 to 1000 volts.

The Adsorption Curve The adsorption of thorium B from solution follows the general adsorption law: As the amount of adsorbing material increases, the adsorption of the radioactive material does not increase in a direct ratio. The relation is expressed approximately by the equation of Freundlich, called the *adsorption isotherm:*

$$x = a \cdot C^{1/n}$$

x = amount adsorbed by unit mass of the adsorbing material
C = concentration, at equilibrium, after adsorption
a and n are empirical constants

It is therefore necessary to determine an adsorption curve for each material studied. This is done by determining the adsorption of thorium B from equal amounts of solution (20 cc.) by progressively increasing amounts of the coarser sample. If at the same time the adsorption by other samples of different degrees of fineness is determined, the surface relations of all the samples can be determined.

The Determination of the Ratios of the Surfaces of Various Samples of Quartz

Quartz sand was ground in a ball mill and then separated with sieves into several fractions, but in no fraction was separation necessarily complete. The samples were designated as follows: *A*, coarser than 40 (the unground sample); *B*, 100–150-mesh; *C*, 150–200-mesh; *D*, through 200-mesh. These treated as described above gave the following data:

TABLE II

No.	Sample	Grams	"Seconds drop"	No.	Sample	Grams	"Seconds drop"
1	*A*	1.000	35.5	5	*B*	0.800	140
2	*B*	0.200	73.5	6	*C*	0.200	95
3	*B*	0.400	104	7	*D*	0.200	107
4	*B*	0.600	126	8	(blank)	.....	16

From this table we could calculate the per cent thorium B adsorbed by each sample as shown in Table I, and an adsorption curve could then be drawn from Nos. 2, 3, 4, and 5, plotting the per cent thorium B adsorbed against the respective weights of the quartz, sample *B*, and on this curve, points for Nos. 1, 6, and 7 could be located and their surface areas evaluated in terms of *B*. Drawing such a per cent adsorption curve would have the advantage that corrections could be made directly for the natural leak of the electroscope as shown in Table I. Since, however, the leak amounted to 100 divisions in 3120 seconds, or 0.032 divisions per second, we can readily correct for this leak by multiplying the "seconds drop" by 0.032 and subtracting this product from the uncorrected reading. If, however, the time in seconds as given in the last column is not much above 125 the error introduced by disregarding the natural leak is well within the experimental error.

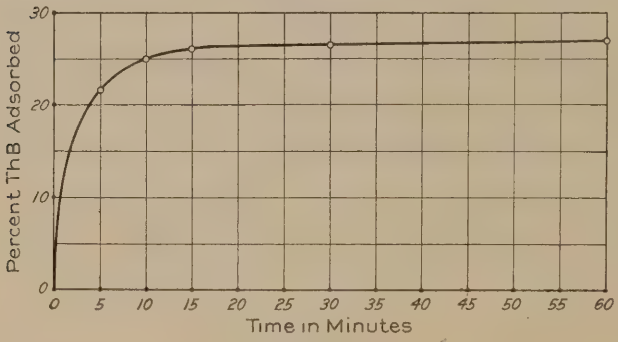

FIG. 1.

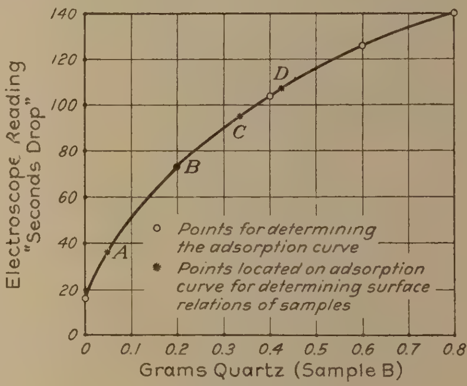

FIG. 2.

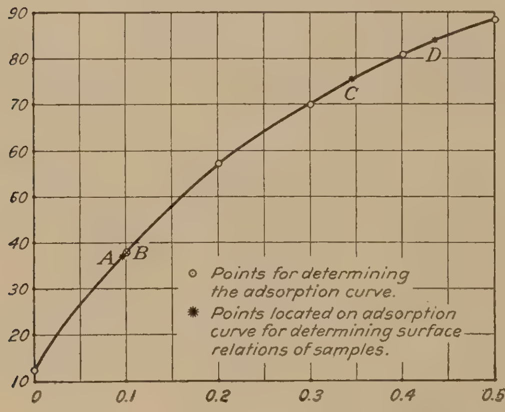

FIG. 3.

Instead of plotting a per cent adsorption curve as in Fig. 1, we can plot directly the "seconds drop" against the respective weights of sample *B*. This gives the curve as shown in Fig. 2. On this curve we can locate the points for samples *A*, *C*, and *D*. The curve shows that 1.000 gm. of *A* has the same adsorption and therefore the same surface as has 0.05 gm. of *B*, or in other words, *B* has twenty times the surface area of *A*. Likewise we find that 0.20 gm. of *C* has the same adsorption as 0.335 gm. *B*, and 0.20 gm. *D* has the same adsorption as 0.425 gm. *B*. From these values we establish the relation:

The surface of *A* : *B* : *C* : *D* : : 1 : 20 : 33.5 : 42.5

As a check, a complete second determination was made. In this, the weights of *B* for the adsorption curve could be selected more judiciously, for from Fig. 2 it is seen that it is not necessary to determine the curve beyond 0.5 gm. quartz, and that by doubling the amount of *A*, its "seconds drop" reading is brought higher on the curve. The results of this second determination are given in Table III and Fig. 3.

The curve shows that 2.00 gm. of *A* has the same surface as 0.097 gm. *B*, or *B* has 20.6 times the surface of *A*. From the second determination the ratios of the samples are:

The surface of *A* : *B* : *C* : *D* : : 1 : 20.6 : 35.5 : 44.8

TABLE III

No.	Sample	Grams	"Seconds drop"	No.	Sample	Grams	"Seconds drop"
1	*A*	2.000	37	6	*B*	0.500	88.5
2	*B*	0.100	38	7	*C*	0.200	75.5
3	*B*	0.200	57.3	8	*D*	0.200	84
4	*B*	0.300	70	9	(blank)	.....	12.5
5	*B*	0.400	81				

It is possible in the case of this sample of quartz to determine the specific surface with a fair degree of approximation. Using the unground sample as a basis, and assuming the particles to be spherical (Fig. 4) we can determine the area per gram. This could be done by the usual method with a microscope equipped with a micrometer eyepiece, but the writer believes the following method to be more accurate:

0.100 gm. of quartz contains 286 grains of sand
Specific gravity of quartz = 2.653
Vol. of 0.100 gm. = 0.03768 cc.
Average vol. per grain = 0.00013175 cc.
Surface = $\pi(6V/\pi)^{2/3}$ = 0.01247 sq. cm. per grain
0.01247 x 286 = 3.57 sq. cm. per 0.100 gm.
= 35.7 " " " gram

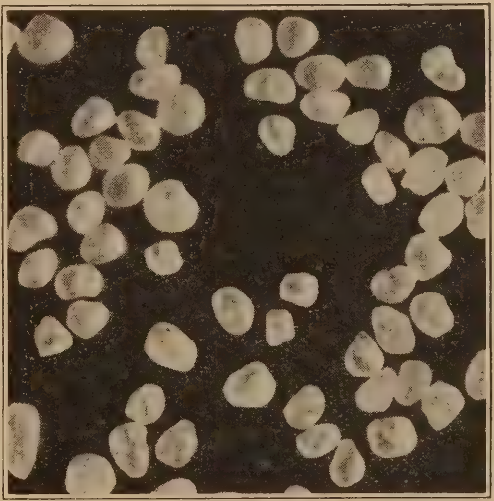

FIG. 4.

From this we calculate the specific surface of the various samples to be as follows:

A—(the unground sand)	36	*C*—(150–200-mesh)	1270
B—(100–150-mesh)	735	*D*—(through 200-mesh)	1600

As seen from Fig. 4, the grains of sand are not perfect spheres, and our degree of error in assuming them to be so is unknown. But there is little doubt that applying a similar or a microscopic method to the ground samples, the error would be very much greater. But as outlined above, we can determine the specific surface of silica of any degree of fineness and of particles of any irregular shapes with practically the same degree of accuracy as we can for the rounded sand particles.

Surface of Other Materials

Typical adsorption curves have been obtained for the following materials: feldspar, zinc oxide, tin oxide, calcite, bone ash, clays, silicon carbide, fused alumina, silica gel, aluminum hydroxide gel, ferric oxide gel, charcoal, and Portland cement.

Some substances like silica and silicon carbide do not adsorb thorium B from aqueous solution in measurable quantities, regardless of their degree of fineness. It was found that concentrated ammonium hydroxide solution added to the solution of thorium B (about 2 cc. per 100 cc. of solution) increased the adsorption by the powdered material to such an extent that adsorption curves could easily be obtained. For substances that form hydrates or are otherwise acted upon by water, ethyl alcohol serves as an excellent solvent for thorium B.

Conclusion on Method

One would judge that the relative surfaces of all granular materials could be determined if an adsorption curve could be obtained. This is probably true of all strictly granular non-porous materials. For kaolin, however, although it gives a typical adsorption curve with water as the solvent for thorium B, equal weight samples of different degrees of fineness all showed the same adsorption, probably due to the particles all slaking and breaking down to similar sizes in all samples.

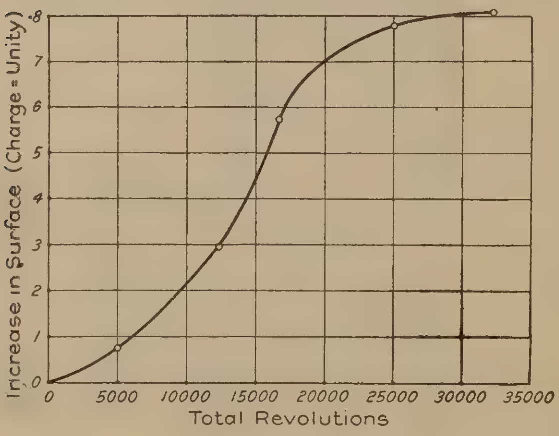

FIG. 5.

Using anhydrous alcohol in place of water, we have a liquid that has no slaking action on clay, and a similar adsorption curve was obtained, but results for different degrees of fineness were erratic. The clays will require further study.

The method as outlined above is limited to the relative surface determination of samples of the same nature. If we can determine the specific surface of one of the samples by one of the more laborious methods as microscopic measurement or sedimentation (Odén), we can with equal accuracy obtain the specific surface of all degrees of fineness of that material. If the relative adsorptive powers for thorium B by different kinds of material are known, then the relative surfaces can be determined among these various samples; and if the relative adsorptive power of lead sulphate can also be determined, then we have available a means of easily determining the specific surface of all powdered materials whose adsorptive power for thorium B is known. These latter problems still remain to be solved.

Application

It may not be amiss to give an example of an application of surface area measurements as outlined above. We now have ball mill studies in progress to determine conditions favorable for most efficient grinding. The relative efficiencies are determined from curves in which increase in surface area of the charge is plotted against number of revolutions of the mill. The curve for one condition of operation is given in Fig. 5.

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THE USE OF GEORGIA AND NORTH CAROLINA KAOLINS IN A SEMIPORCELAIN BODY

By S. E. Hemsteger and W. C. Stief[1]

ABSTRACT

Tables are given, comparing properties and analyses of Georgia and North Carolina kaolins and two English china clays. These two domestic clays are found to be very adaptable to this type of body. North Carolina kaolin reduced warping of ware in the glost kiln, but made the body less plastic. Georgia kaolin enabled a higher flint content to be used, also imparted greater dry strength to the body. Since using these domestic kaolins, crazing has been reduced.

There has not been a great amount of material published on the practical use of these two American clays. The use of North Carolina kaolin has been quite extensive while the use of Georgia kaolin has been used to lesser extent by some manufacturers of semiporcelain dinnerware. This paper is concerned with notes and results of the use of these two domestic clays in a semiporcelain plastic body for making dinnerware.

Table I gives the approximate properties of Georgia kaolin, North Carolina kaolin, and two well known English china clays for comparison. Table II gives the chemical analyses of these same four clays.

Table I

Name	% Drying shrinkage	% Firing shrinkage cone 8	% Total shrinkage	Modulus of rupture (dry)	% Residue on 200-mesh screen	% Absorption at cone 8
Georgia kaolin	3.8	8.1	11.5	132	0.53	17.59
N. Carolina kaolin	2.2	4.3	6.7	25	2.96	32.69
"A" Eng. china clay	2.7	8.1	10.5	41	0.20	22.35
"B" Eng. china clay	4.8	10.8	15.1	83	0.26	15.41

Table II

		Georgia kaolin	N. Carolina kaolin	"A" English china clay	"B" English china clay
Silica	SiO_2	45.58	47.43	41.54	41.66
Loss on ignition		13.96	12.12	12.46	12.50
Alumina	Al_2O_3	38.97	34.47	45.10	45.25
Ferric oxide	Fe_2O_3	0.62	0.64	0.76	0.55
Calcium oxide	CaO	0.51	0.02	0.10	Trace
Magnesium oxide	MgO	0.36	0.07	0.02	Trace
Potassium oxide	K_2O		1.18	0.04	Trace
Sodium oxide	Na_2O		0.02		0.06
Titanium oxide	TiO_2		0.02		
Phosphorus pentoxide	P_2O_5		0.04		
Moisture at 105°C			4.05		
		100.00	100.06	100.02	100.02

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (White Wares Division.)

The fired color of the North Carolina kaolin is quite good while that of the Georgia kaolin is very slightly inferior to the English china clays. This Georgia kaolin has a slightly yellowish cast. In our experience the American clays come with practically as good a uniformity as the English clays.

Laboratory body tests using large percentages of these American clays proved their adaptability to this kind of body. Their use on a practical basis was begun and the results closely scrutinized from the mixing to the finished product.

We have found these domestic clays very adaptable to a plastic semiporcelain body, but there are limits to their use and they necessitate a rearrangement of the body batch. Domestic clays have been condemned, due to their substitution for imported clays, pound for pound. Consideration must be taken of the fact that some of these clays have different physical structure and properties unlike the English clays.

North Carolina kaolin produces a better colored body and has the property of helping to reduce warping of the ware in the glost kiln to a great extent. Its use is limited however, due to its rapid drying and chiefly its tendency to "shorten" the body resulting from its non-plastic nature. The open-firing qualities of this clay can be counteracted by the increase of feldspar content or higher heat in the bisque kiln.

The use of Georgia kaolin has permitted increase in the flint content and at the same time the dry cross-breaking strength has been greatly increased. Since using these domestic clays, crazing has been considerably reduced, clay ware loss and bisque loss have held at a low point and glost thirds have been greatly decreased. Any slight inferior color, due to the Georgia kaolin, can be counteracted by a slight increase of the cobalt stain content.

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THE MECHANISM OF SPALLING[1]

By F. H. Norton[2]

ABSTRACT

A study has been made of the stresses and fractures developed in a solid when rapidly heated or cooled. The stresses were measured in bakelite specimens by the photoelastic method. High stresses in all cases were found to occur near the surface of the solids, but no high tension stresses were present when the specimens were being heated. A number of vitreous clay spheres and bricks were heated and cooled rapidly and the nature of the cracks was noted. In practically every case the fractures occurred as predicted from the measured stresses. Torque-deflection curves were obtained for a number of fire brick in torsion at different temperatures. The temperature at which plastic flow occurs for every material tested was approximately the same as the temperature of the initial deflection under compressive loads in a standard load test.

I. Introduction

In a previous article[3] I developed a theory of spalling based on the assumption that all spalling fractures were due to shear stresses. The validity of this assumption has been questioned on a number of occasions, but there seemed to be little or no data available to show the type of temperature stresses occurring in a solid. Therefore, to inquire more closely into the mechanism of spalling and the applicability of the previous theory, the stresses and the method of fracture were studied on a number of solids under varying temperature conditions. Heretofore, spalling has generally been measured by a number of cycles of heating and cooling, and generally no distinction has been made between the stresses due to heating and the stresses due to cooling. As it seemed quite probable that the stresses on heating would be different from those on cooling, the two have been separated in the following tests by heating suddenly and cooling very slowly, or by heating slowly and cooling suddenly.

If the fracture due to temperature changes is caused by shear stresses, then according to the theory just referred to, the spalling, S, of a material is proportional to:

$$\frac{\Delta}{h\phi}$$

where
Δ = the coefficient of expansion
h = the (diffusivity)$^{\frac{1}{2}}$
ϕ = the maximum shearing strain

On the other hand if a fracture is caused by tension stresses the

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[1] Received March 20, 1926.

[2] Babcock & Wilcox Fellow, Division of Industrial Coöperation and Research, Mass. Institute of Technology.

[3] "A General Theory of Spalling." *Jour. Amer. Ceram. Soc.*, **8**[1], 29–39(1926).

tendency to spall is given by the formula of Winkelmann and Schott:[1] where

$$S=\frac{p\sqrt{k}}{E\sqrt{\rho c}}$$

S = the tendency to spall
p = the tensile strength
k = the heat conductivity
Δ = the coefficient of expansion
E = the modulus of elasticity
ρ = the density
c = the specific heat

It will be seen that this equation reduces to the same form as the one given above because:

$$h=\frac{\sqrt{k}}{\sqrt{\rho c}}$$

and the maximum tensile strain:

$$e=\frac{p}{E}$$

therefore

$$S=\frac{\Delta}{he}$$

The manner in which a brick will spall, assuming no compression failure, depends on the relative value of the maximum shear and tensile stresses and on the ratio $\frac{\phi}{e}$ for the material used.

The value of the stresses can be determined by the photoelastic method as described later. The value of e and ϕ for brittle materials, especially at high temperatures, is not easy to determine. Attempts have been made to measure ϕ by applying torsion to a square bar but it is not certain that the fractures are due to shear stresses for the break is often on a 45° spiral, indicating a tension rather than a shear failure. It seems reasonable to believe however that the ratio of $\phi : e$ is approximately constant for brittle materials such as occur in ceramics. It is quite possible however that the ratio might change when the temperature is sufficiently high to make the material somewhat plastic.

II. The Distribution of Temperature Stresses in Solids

The distribution of stresses in solids has been studied recently by the photoelastic method where the stress distribution is too complicated for mathematical analysis. This method has been used for such problems as measuring the stress distribution in eye-bolts, hooks, gear teeth, and ship hulls, but it has been used little if any, for the measurement of temperature stresses. This particular investigation of temperature stresses was carried out by Dr. Paul Heymans and T. H. Frost in the Photoelastic Laboratory, Department of Physics, at the Massachusetts Institute of Technology.

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[1] "Ueber thermische Widerstandskoeffizienten verschiedener Glaser in ihrer Abhängigkeit von der chemischen Zuzammensetzung," *Ann. der Phys. u. Chem.*, **51**, 730 (1894).

As the photoelastic method is not generally understood, and most of the descriptions are of a rather mathematical nature, it is believed that a brief description of the photoelastic theory will not be out of place here. The method is based on the fact that when a beam of polarized light is passed through an isotropic substance without strain the beam is unaltered, but when the substance is strained it becomes anisotropic and the beam suffers double refraction and is split up into an extraordinary and an ordinary ray, which when turned into the same plane by an analyzer, interfere and produce bands of color. The phase difference between the interfering rays is proportional to the amount of stress in the material and the stress optical constant for that material.

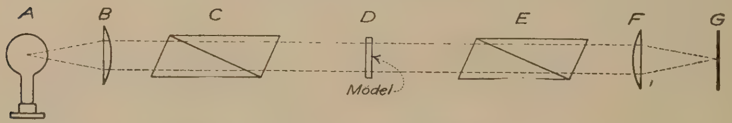

FIG. 1.—Apparatus for photoelastic measurement.

The apparatus used for making photoelastic studies is shown in Fig. 1. *A* is a source of white light which is brought into a parallel beam by the lens, *B*, and is then circularly polarized by the nichol prism *C*. The circularly polarized beam then passes through the specimen *D* under test, through the analyzing nichol, *E*, and is focused by the objective, *F*, onto the ground glass of the camera, *G*. When an unstrained specimen is in place, its image appears entirely of a neutral tint, but when stresses occur, colored bands appear covering the whole range of the spectrum, and if the stresses are high these bands will be repeated a large number of times in spectra of different orders.

These bands do not represent the stresses directly, but only the difference between the two principal stresses, p and q, because the colors are caused by the path difference of the two rays formed by the principal stresses, p and q. If a line be drawn over the image along one band of color, it will be known as an isochromatic line and will represent a line of equal maximum shear; for the maximum shear is proportional to one-half the difference of the principal stresses.

So far we have obtained only the values of the shear stresses. To obtain the separate values of the principal stresses we must know their direction at every point. We can obtain this information from the isoclinic lines which are lines of equal direction of principal stresses. These lines are obtained with plane polarized light in place of circularly polarized light, by rotating the analyzer through various angles so that the isoclinic lines, which appear as dark bands, can be determined from the image. The values of the principal stresses can be obtained from the isochromatic and isoclinic lines by the method described by Professor Filon.[1]

To study the temperature stresses it was considered necessary to use models of a material having a high stress-optical constant, as the temperature stresses are relatively low. For this purpose, sheet bakelite about 10 mm. thick was used. This material was as free as possible from initial stresses, although there was aways some coloration in the unstressed model. The specimens were accurately cut to the proper size and mounted as shown in Fig. 2, in a brass holder through which steam or ice-water could be passed. In order to prevent the expansion or contraction of this holder from interposing stresses on the model, a layer of metal filings was placed between the edge of the model and the holder in such a way as to allow rapid conduction of heat but no transfer of pressure.

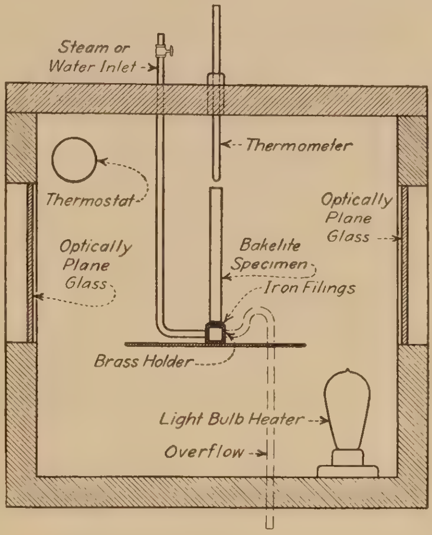

FIG. 2.—Constant temperature chamber.

The model and its holder were mounted in a chamber which was maintained at a constant temperature of 50°C by means of a thermostat, and the beam of light passed through optical glass windows at the end of the chamber. The method of conducting the test consisted in adjusting the model in the constant temperature chamber and allowing it to remain there until it had reached equilibrium, then either steam or ice-water was allowed to flow suddenly through the holder. The development of the isochromatic lines was then carefully watched on the ground glass of the camera. In about 45 seconds the stresses had reached their maxima at which time an autochrome plate was slipped into the camera and an exposure taken. Immediately afterwards the isoclinic lines were observed and sketches made of them. Autochrome plates were also taken of the unstrained specimen to determine the initial stresses.

From these plates and sketches and the constants of the bakelite, the stresses were computed. The precision of these measurements was not great, due to the rapidity with which the stresses changed and to the initial strains which were present in most of the models. For this reason it is not believed that the absolute values of the stresses have been determined to much better than ±20%. However, the distribution of the stresses, which is what we are most interested in, should be relatively more precise.

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[1] Engineering, Oct. 19, 1923.

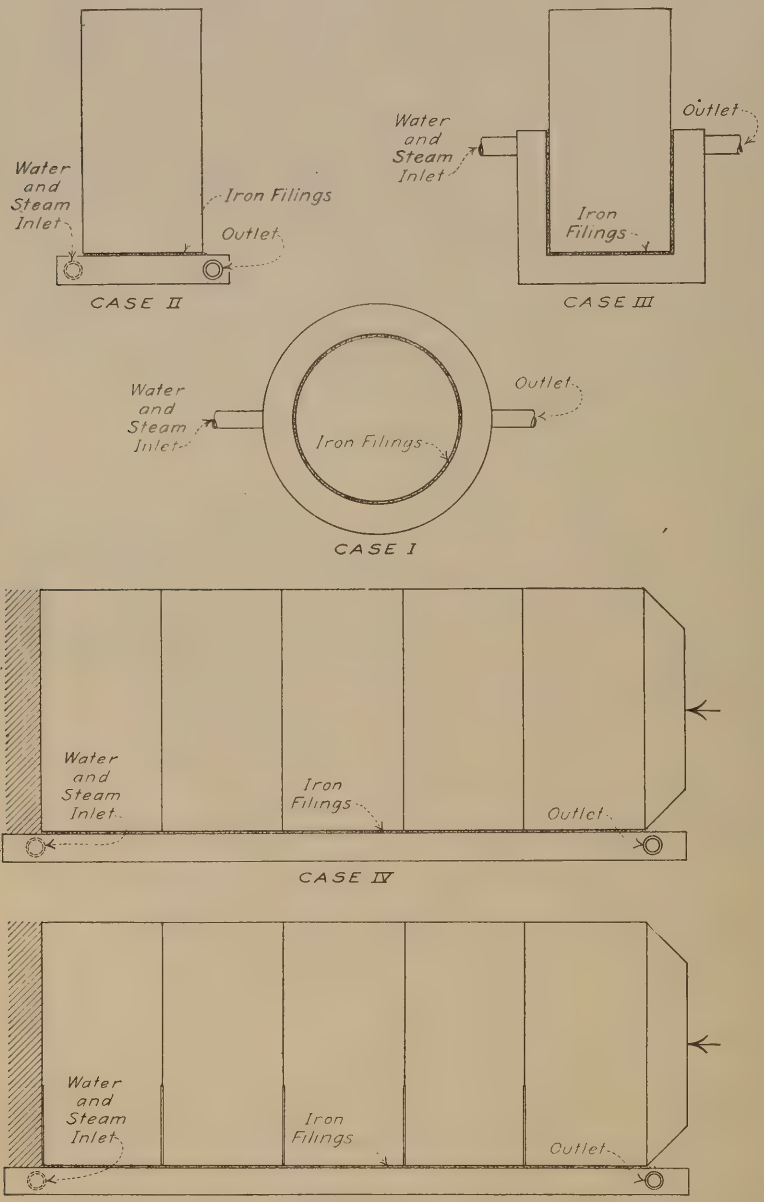


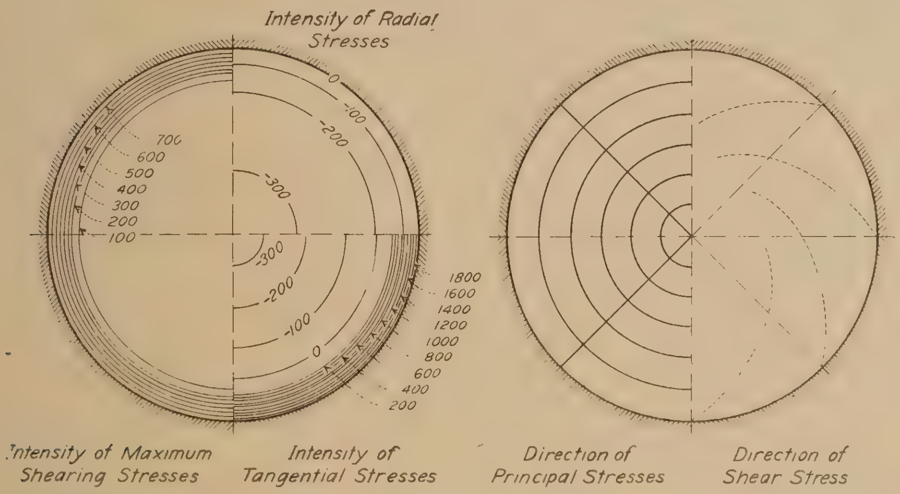
FIG. 3.—Mounting of the models.

The first object examined was a sphere because of its simplicity. Its model (I, Fig. 3) was made out of sheet bakelite in the form of a disk approximately 70 mm. in diameter. In the first test the temperature around the edge was suddenly increased from 50 to 100°C and in the second test it was suddenly decreased from 50 to 0°C. The isochromatic lines began at the edge and gradually worked in until they reached their maximum number. In all cases the isochromatic lines were concentric with the center of the disk.

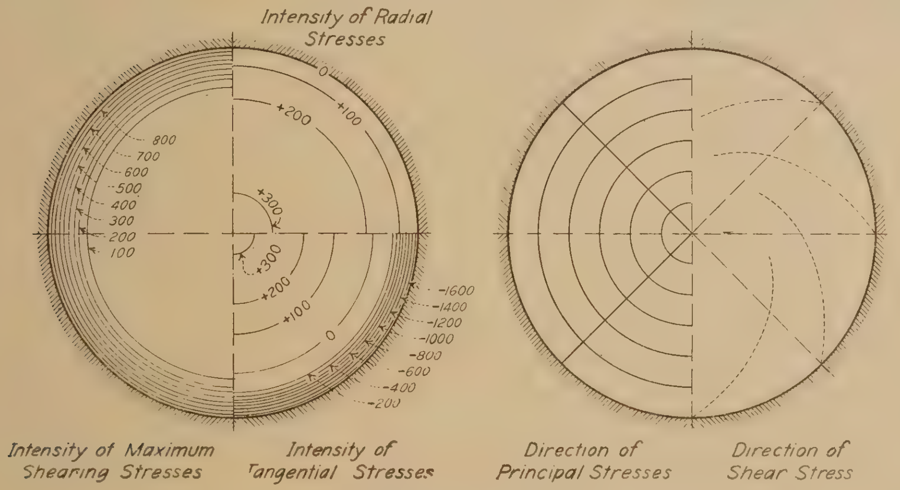
The second specimen to be tested was a brick heated on one end. A model (II, Fig. 3) was made of bakelite approximately 37 x 75 mm. The edge was heated and cooled as before.

The third specimen was a brick, a model (III, Fig. 3) of which was identical to the preceding one but in this case it was heated on the end and one-half the way up each side to more or less simulate the conditions in a spalling test.

The fourth specimen tested consisted of a brick compressed lightly between other similar brick all of which were heated on the ends as shown in IV, Fig. 3. This was to simulate conditions in a wall.


Intensity of Radial Stresses
0
-100
-200
-300
700
600
500
400
300
200
100
-300
-200
-100
0
1800
1600
1400
1200
1000
800
600
400
200
Intensity of Maximum Shearing Stresses
Intensity of Tangential Stresses
Direction of Principal Stresses
Direction of Shear Stress

SURFACE HEATED


Intensity of Radial Stresses
0
+100
+200
+300
800
700
600
500
400
300
200
100
+300
+200
+100
0
-1600
-1400
-1200
-1000
-800
-600
-400
-200
Intensity of Maximum Shearing Stresses
Intensity of Tangential Stresses
Direction of Principal Stresses
Direction of Shear Stress

SURFACE COOLED

FIG. 4.—Stresses in a sphere.

In the fifth case the model was identical with the preceding one except the sides of the model bricks were slightly relieved $\frac{1}{3}$ of the distance from the end as shown in V, Fig. 3. This was done in order to determine the effect of allowing the heated end of each brick to expand and contract without restraint.

The results of this stress investigation are plotted in Figs. 4 to 8. It was believed that the stresses could be portrayed most clearly by showing a cross-section of the specimen and plotting upon it lines of equal stress. This has been done for the maximum shearing stress, the resultant tension and compressive stresses, normal and parallel to the longitudinal axis of the specimen. It should be noticed that these resultant stresses are identical with the principal stresses throughout most of the area of the specimen and only differ from them in the corners where the direction of the principal stresses is altered. The resultant stress in any desired direction is obtained from the equation:

$$R = p \sin^2\alpha + q \cos^2\alpha$$

where

R is the resultant stress
p and q, the values of the principal stresses
α, the angle between the principal stresses and the resultant

The values for the stresses are the values obtained on the bakelite model with a temperature change of 50°C and have no relation to the absolute values of stress occurring in a refractory. All that is intended to show by the curves is the distribution of stress in the model.

The direction of the shearing and the principal stresses is also shown in the figures in order to correlate the direction in which the stresses act with actual fractures described later.

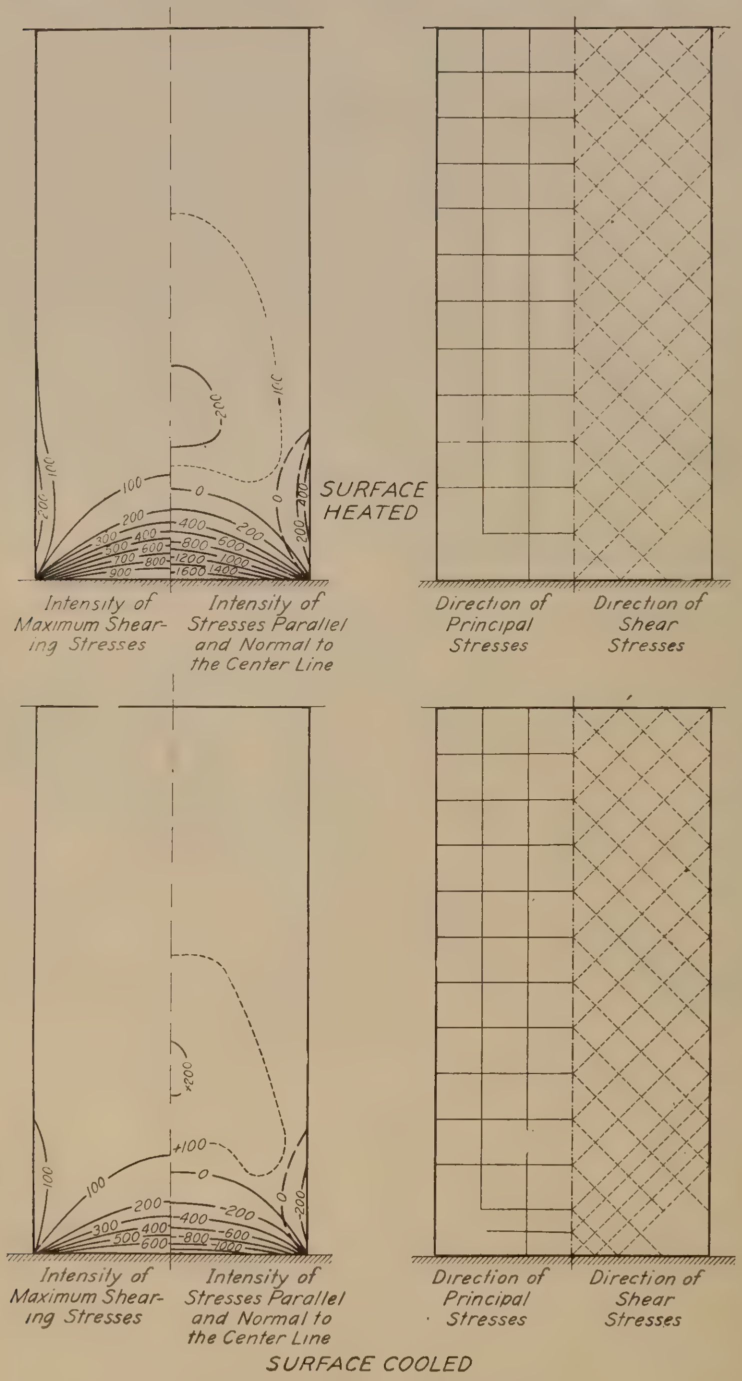

SURFACE HEATED
Intensity of Maximum Shearing Stresses
Intensity of Stresses Parallel and Normal to the Center Line
Direction of Principal Stresses
Direction of Shear Stresses
100
200
300
400
500
600
700
800
900
0
-200
-100
400
800
1200
1600
200
600
1000
1400
Intensity of Maximum Shearing Stresses
Intensity of Stresses Parallel and Normal to the Center Line
Direction of Principal Stresses
Direction of Shear Stresses
SURFACE COOLED
+100
+200
0
-100
100
200
300
400
500
600
-200
-400
-600
-800
-1000

FIG. 5.—Stresses in a brick.

In all of the figures compression stresses have been arbitrarily designated as positive, and tensile stresses as negative. There has been no sign attached to the shearing stresses as it would have no significance in this problem.

Case I represents a section through a sphere. On heating, high compressive stresses are developed near the surface in a tangential direction but these rapidly diminish to zero at about one-fourth of the distance toward the center, leaving tensional tangential stresses in the central area of rather small magnitude. The radial stresses which are zero at the surface slowly increase to a maximum at the center where they are of the same magnitude as the tangential stresses. It will therefore be seen that the center of the sphere is under a negative static pressure as the stresses are equal in all directions. The shearing stresses are a maximum at the surface where they have a direction 45° from a radius. These stresses gradually diminish until they reach zero near the center of the sphere which naturally follows from the fact that principal stresses are equal in this region. When the sphere is cooled at the surface the stresses are approximately the same as in the preceding condition but with a reversed

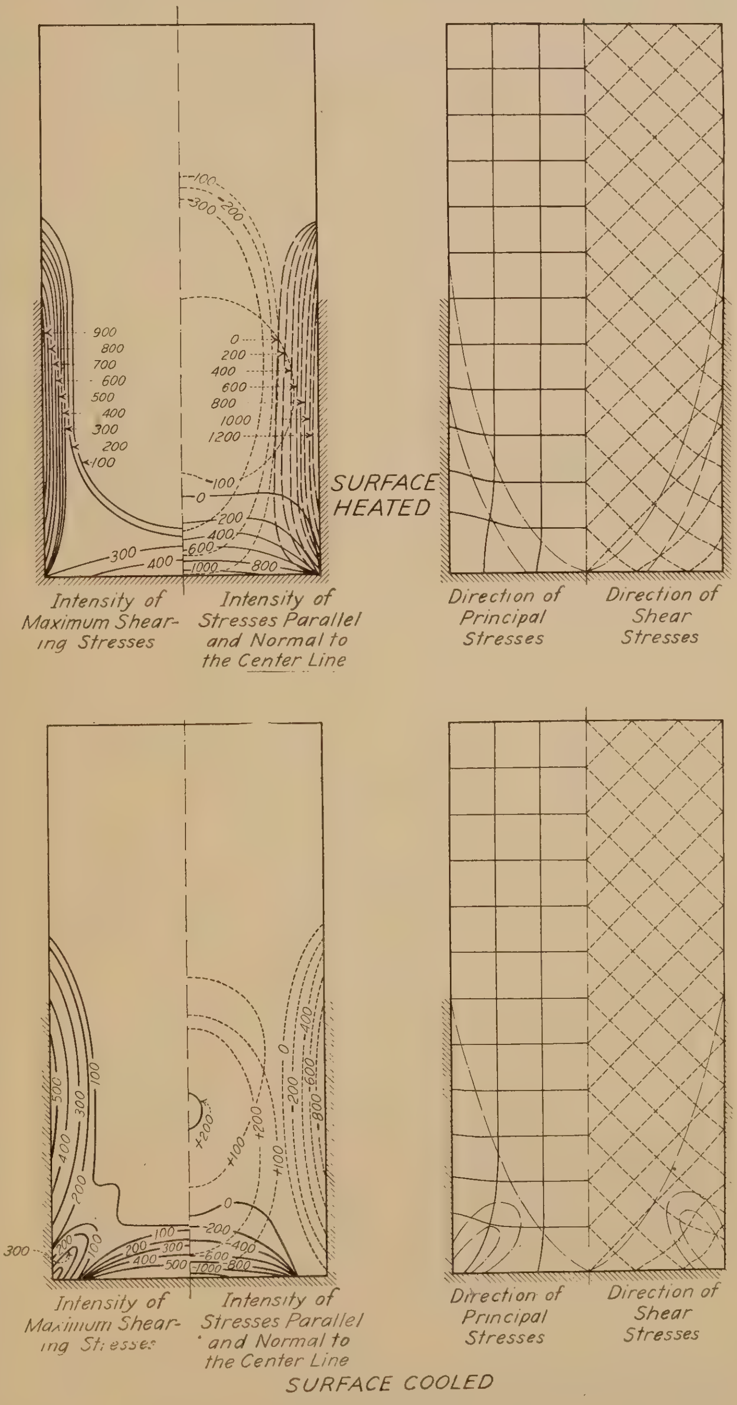

Intensity of Maximum Shearing Stresses
Intensity of Stresses Parallel and Normal to the Center Line
Direction of Principal Stresses
Direction of Shear Stresses
SURFACE HEATED
Intensity of Maximum Shearing Stresses
Intensity of Stresses Parallel and Normal to the Center Line
Direction of Principal Stresses
Direction of Shear Stresses
SURFACE COOLED

FIG. 6.—Stresses in a brick.

sign. Here the skin of the sphere is highly stressed in tension while the interior is compressed equivalent to a hydrostatic pressure. The shearing stresses have the same direction and approximate magnitude as for the condition of heating.

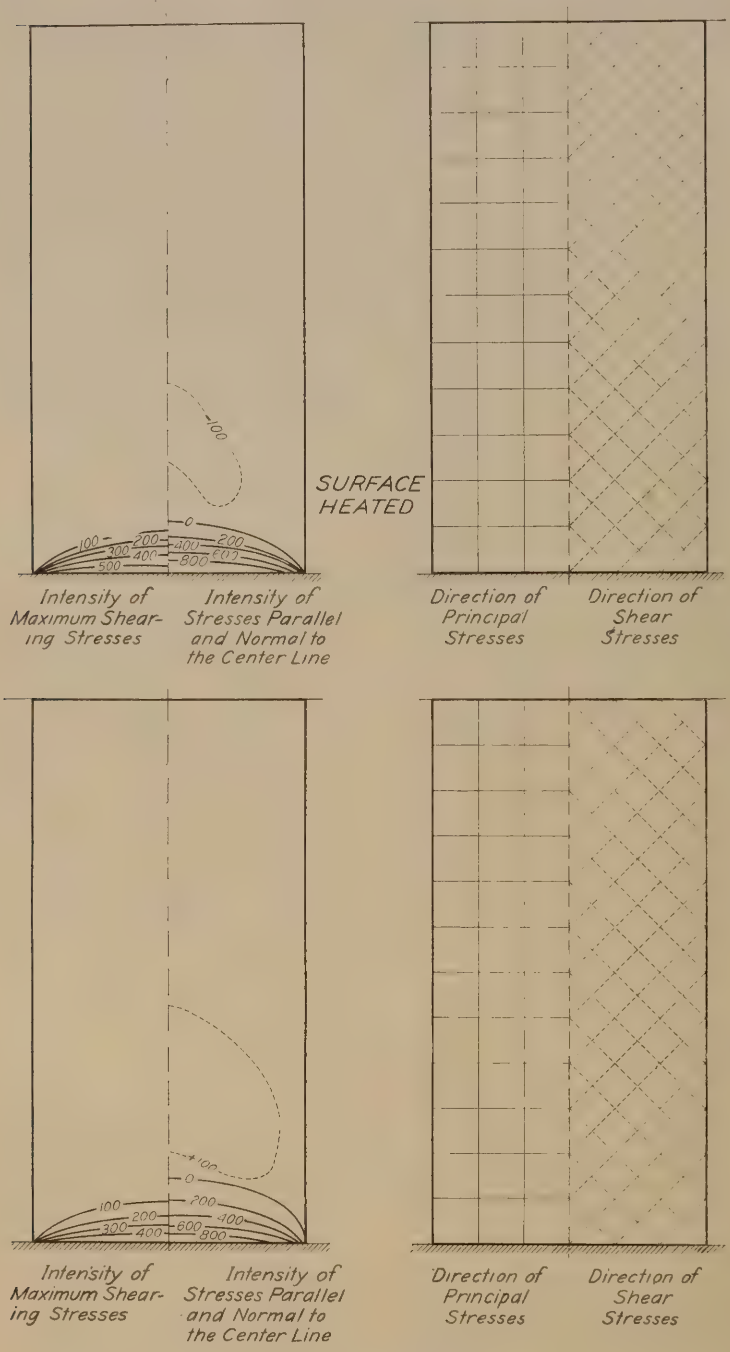

100
0
100
200
300
400
500
200
400
800
600
200
SURFACE HEATED
Intensity of Maximum Shearing Stresses
Intensity of Stresses Parallel and Normal to the Center Line
Direction of Principal Stresses
Direction of Shear Stresses
100
0
100
200
300
400
200
400
600
800
Intensity of Maximum Shearing Stresses
Intensity of Stresses Parallel and Normal to the Center Line
Direction of Principal Stresses
Direction of Shear Stresses
SURFACE COOLED

FIG. 7.—Stresses in a wall.

In Case II a brick is represented with temperature changes occurring only on the end. In the condition where the end is suddenly heated, the shearing stresses reached a maximum of 1000 pounds per square inch at the center of the end and smaller maxima appear a short distance up the sides of the brick. The direction of these shearing stresses are 45° from the axis of the specimen. The resultant stresses normal to the longitudinal axis reached a value of 1800 pounds per square inch (compression) at the center of the end and reached a zero value about two-tenths of the distance up the axis. There is an area of tension in the center of the brick. The stresses parallel to the longitudinal axis, as we should expect, are small and occur a short distance up the side of the brick. Under the conditions where the brick is cooled the stresses are distributed in much the same manner except that they are slightly lower and have the opposite sign giving a maximum tension of 1200 pounds per square inch at the center of the end.

In Case III the brick is heated on the end and part way up the sides. This method of heating increases the shearing stresses at the sides of the brick to 1000 pounds per square inch and decreases them on the end to 500 pounds per square inch. It is also interesting to notice that the direction of the principal stresses has been considerably changed at the corners of the brick, resulting in a marked curve of the lines of shear stresses. This fact is of importance as will be shown later when the fracturing of a brick is discussed. The resultant stresses normal to the axis are considerably decreased and a smaller negative area is observed. The resultant stresses parallel to the axes are increased to 1600 pounds per square inch and the negative area is considerably augmented. Under the conditions of cooling the distribution of stresses is similar except that the sign is changed; however, it will be noticed that there is a small region of stress at the corners under these conditions which does not appear in any other test.

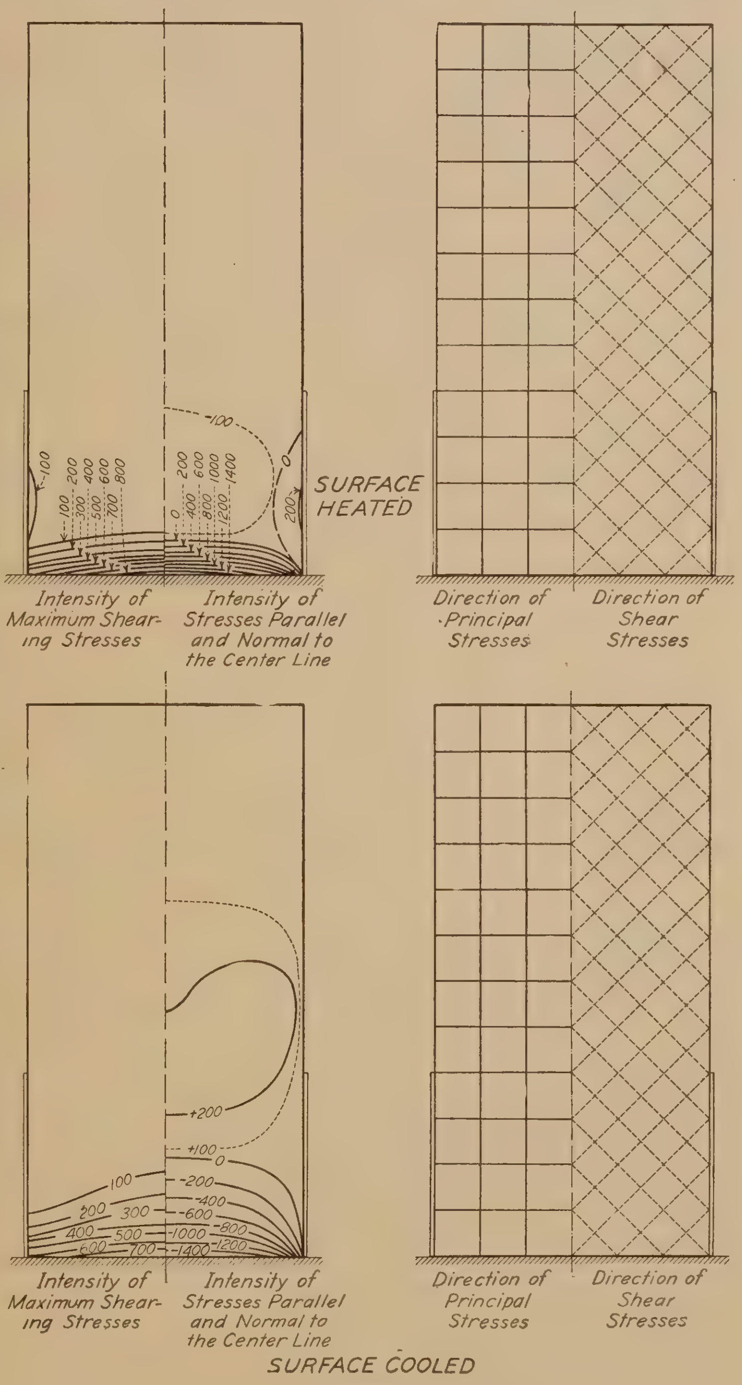

-100
100
200
300
400
500
600
700
800
-100
0
200
400
600
800
1000
1200
1400
0
200
SURFACE HEATED
Intensity of Maximum Shearing Stresses
Intensity of Stresses Parallel and Normal to the Center Line
Direction of Principal Stresses
Direction of Shear Stresses
100
200
300
400
500
600
700
+200
+100
0
-200
-400
-600
-800
-1000
-1200
-1400
Intensity of Maximum Shearing Stresses
Intensity of Stresses Parallel and Normal to the Center Line
Direction of Principal Stresses
Direction of Shear Stresses
SURFACE COOLED

FIG. 8.—Stresses in a wall.

In Case IV the specimen represents a brick held between other similar bricks as in a wall. The shearing stresses reached a maximum of 900 pounds per square inch at the end and were nearly constant across the end of the brick. The resultant stresses normal to the axis reached 1600 pounds per square inch at the end. The resultant stresses parallel to the axis are quite small due to the fact that the isothermal lines are nearly parallel to the brick. The conditions of cooling give similar stresses but with opposite sign.

In Case V, the end of the brick is free from its neighbors which prevents transference of stress from one brick to another but makes the isothermal lines nearly parallel to the surface. On heating, the shearing stresses occur only at the heated end but differ from the preceding case in becoming zero at the corners as we should expect. The resultant stresses normal to the axis are rather small as they only reach 1000 pounds per square inch. The resultant stresses parallel to the axis are zero in all cases. Under the conditions of cooling the stresses are the same except for the change in sign.

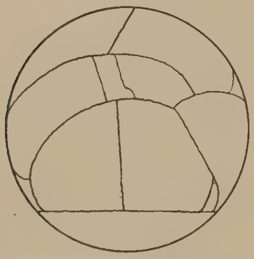


FIG. 9.—Cracks in suddenly heated sphere.

We may conclude from the preceding results that:

1. The stresses set up in a solid by suddenly heating the surface through a certain temperature interval are of the same order but of opposite sign from those set up by cooling the surface through the same temperature difference. In the preceding experiments the heating stresses are uniformly higher than the cooling stresses but this is due undoubtedly to the fact that the temperature was raised much more suddenly by steam than it was reduced by ice-water.

2. There are no high tensile stresses developed on sudden heating.

3. The maximum shearing stresses are approximately equal to one-half the maximum resultant stresses.

4. The resultant stresses are generally low at the corners and the interior of the specimen but reach their highest values along the heated sides at a distance from the corners.

III. Spalling Fractures

A number of spheres were made up of finely-crushed grog and fire clay and fired at such a temperature as to make them vitreous. The diameter of these spheres was approximately 100 mm. and although care was used in molding them, they were not entirely free from flaws and laminations. In the first test, a sphere was suddenly introduced into a furnace at a temperature of approximately 900°C and after it had attained a uniform temperature it was allowed to cool slowly with the furnace. This procedure was repeated twice and then the sphere was examined for cracks which had developed during the sudden heating.

While there were a number of irregularities due to laminations in the spheres in general, the system of cracks was quite definite as shown in Fig. 9. A segment of the sphere having a height of about one-third of the radius was split off so that the angle between the plane of the fracture and the plane tangent to the surface of the sphere at the point of fracture made an angle of 45°. From this fracture other cracks had developed which in turn made the same angle with a tangent to the surface of the sphere. Some of these main divisions or segments were also cracked into smaller pieces more or less at random, but in nearly every case the cracks entered the surface at an angle of 45°. In Fig. 10 is shown a view of the same sphere with a segment removed and it will be noted how the remaining cracks followed this same system.

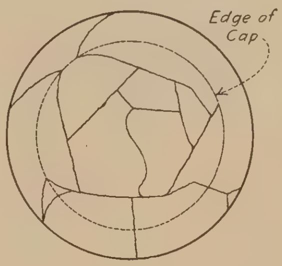


Fig. 10.—Top view of sphere in Fig. 9 with cap removed.

Referring to the diagram showing the stresses developed in a sphere on sudden heating, it is noted that the surface is in compression, which, in itself, would not cause fracture in this material. Therefore the cause of the fracture must be due to shearing stresses and this is confirmed by the fact that their direction coincides with the direction of the maximum shear stresses, which as shown from Fig. 4 approach the surface at an angle of 45°.

Another sphere of the same kind was slowly heated in a furnace to 900°C and then brought suddenly out and allowed to cool in still air. This cycle was repeated twice and the development of cracks observed. In Fig. 11 are shown the principal fractures on the surface of the sphere and it will be at once evident that in general they follow great circles. The fractures extend into the sphere at an angle of 90° to the surface and divide the sphere into a number of parts. This type of fracture is distinctly different from the preceding one and is due undoubtedly to tension stresses set up in the surface of the sphere by the sudden cooling. These stresses are tangential and would tend to fracture the sphere in the observed manner.

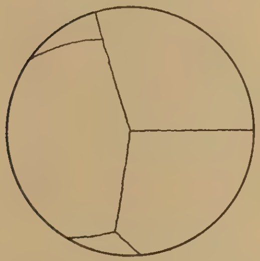


Fig. 11.—Cracks in suddenly heated sphere.

A brick was made up of the same material as the sphere and was suddenly heated as before for about one-third of its length. After three cycles the development of cracks was observed. As shown in Fig. 12

the cracks tended to run across the corners of the brick and in practically every case entered the surface at an angle of approximately 45°. It was also noted that the fractured surface when near a corner was cylindrical or spherical as shown for typical spalls in Fig. 13. Under these conditions of heating the stresses causing fractures were undoubtedly shear stresses as the lines of fracture follow very closely the lines of shear stresses as shown in Fig. 6. Even the curvature at the corners is closely followed.

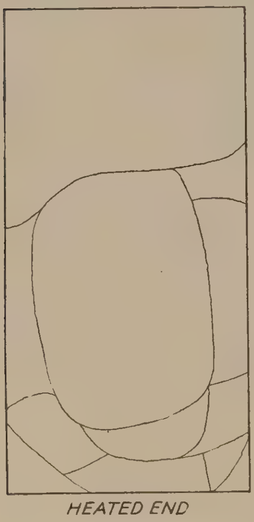


Fig. 12.—Cracks in suddenly heated brick.

A similar brick was heated slowly and cooled rapidly under the same conditions as for the sphere. The type of fracture observed in this case was entirely different from the preceding case as shown in Fig. 14. Here the fractures entered the surface at right angles and tended to divide the brick up into cubes although there were some irregularities due to laminations in molding. Here the spalling is due undoubtedly to the tension stresses developed at the surface. At the edges and corners, shear fractures were also observed in some cases. This is due to the fact that even on rapid cooling the shear stresses are greater than the tension stresses at the corners.

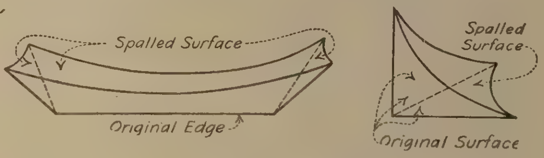


Fig. 13.—Typical spalled fragments.

It was observed in both the case of the sphere and the brick that the fractures due to rapid heating occurred rather suddenly, that is, the piece was split off instantaneously; while in case of the tension cracks under quick cooling conditions it was noted that the cracks started at the surface and penetrated deeper into the brick at each cycle until finally two cracks met and separated a piece.

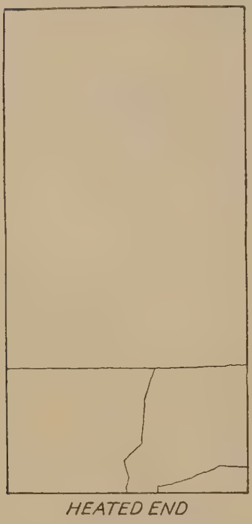


Fig. 14.—Cracks in suddenly cooled brick.

It might be interesting to consider the cracks developed in a brick subjected to the usual spalling test where it is heated on the end and part way up the side in a furnace and then cooled in the same way in an air blast. In Fig. 15 there is shown a typical brick after it has been through a number of heating and cooling cycles. It will be noted that the lower end and corners have lost pieces in such a way as to leave an approximately spherical surface. It will also be noted that half-way up the brick there is a crack dividing it squarely across. It seems quite probable that the spalling of the lower end of the brick is due to shear stresses; first, because the shape of the surface corresponds with the direction of the maximum shearing force, and second, because the fracture corresponds with those produced when a brick was subjected to sudden heating alone. On the other hand the crack across the center of the brick is probably due to tension stresses which are maximum at this point and are due to the cooling.

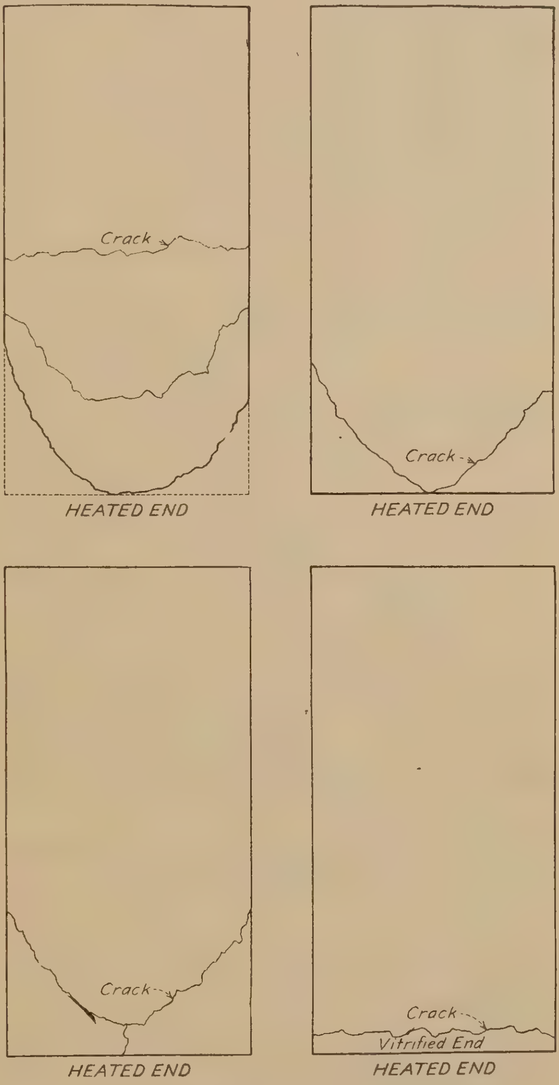


FIG. 15.—Brick from spalling test.
FIGS. 16, 17, and 18.—Brick from furnace wall.

In Fig. 16 is shown a typical spalled brick taken from a furnace wall. It will be noted that the main fractures run at 45° to the surface of the wall and tend to split off the corners of the brick. There can be little doubt that this spalling is due mainly to the shearing stresses. Another type of spall often noticed in bricks removed from the wall is shown in Fig. 17. This is very similar to the last case excepting a short crack in the center of the brick which connects with the 45° fractures. The crack in the end of the brick is probably due to tension stresses which, as can be seen from Fig. 7, are maximum at this point. The other fractures, as in the previous case, are caused by shearing stresses. It cannot be definitely stated in this case which is the primary form of failure.

Another type of spall in service is the separation of a thin layer of brick as shown in Fig. 18. This is generally due to the vitrification of the surface which being more rigid than the original brick, easily cracks off.

IV. The Flexibility of Bricks at High Temperatures

The flexibility of brick in shear was measured for a number of specimens at the low temperature of 500°C in a previous investigation.[1] Since then, similar tests have been made by Booze and Phelps[2] at temperatures up to 800°C where plastic flow began.

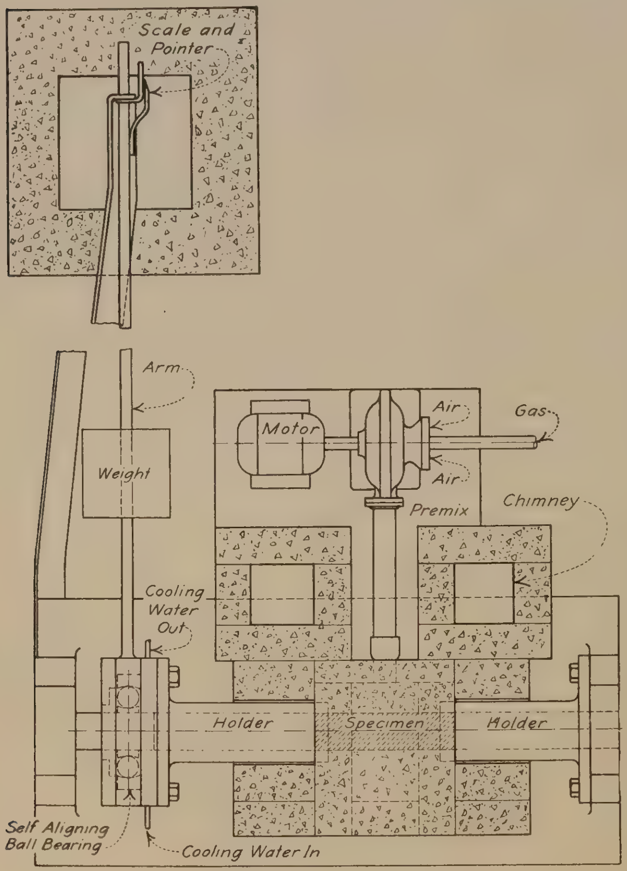


FIG. 19.—Machine for making hot torsion test on refractories.

It seemed desirable to make further tests of this kind on other bricks, so a more powerful testing machine was constructed as shown in Fig. 19. The specimen was $2\frac{1}{2}$ inches square and 9 inches long and was cemented into heavy cast-iron holders which were watercooled. One of the holders was mounted on a self-aligning ball bearing with a moment arm and a sliding weight. A small furnace was built around the specimen and temperatures as high as 1550°C could be obtained over the specimen without difficulty. A test could be made by maintaining a steady temperature and increasing the moment until the desired deflection was obtained or a constant moment could be applied, and the temperature gradually raised as in the standard load test. This latter procedure was followed in making the curves shown in Fig. 20.

Plastic flow began for the Missouri and Pennsylvania brick at approximately 900°C and they deflected rapidly above 1100°C. On the other hand the kaolin brick showed very little deflection up to 1350°C but began to deflect rapidly at 1500°C. It is quite possible that a kaolin brick had no real deflection below 1300°C, as the deflection indicated might have been due to a deflection of the cement or holder.

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[1] "A General Theory of Spalling," *loc. cit.*, **8**, 29–39(1925).

[2] "A Study of the Factors Involved in the Spalling of Fireclay Refractories with Some Notes on the Load and Reheating and the Effect of Grind on Shrinkage," *Jour. Amer. Ceram. Soc.*, **8**, 361–82(1925).

In all of these tests the load was sufficient to give a maximum shearing stress of 25 pounds per square inch in the specimen.

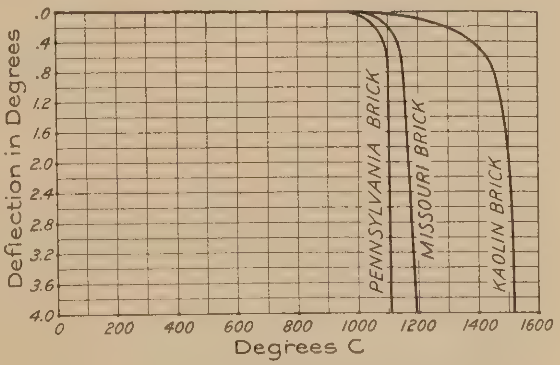

FIG. 20.—Torsion characteristics for various bricks. Deflection vs. temperature under constant load.

When the temperatures at which rapid deflection occurred in this test are compared with the temperatures at which deflection began in a standard load test, it was noticed that they were almost identical.

It seems reasonable to suppose that spalling cannot take place at temperatures above the region where plastic flow occurs, for under these conditions large stresses could not be set up. This is confirmed by observation, as spalling almost always occurs between 400 and 600°C for fireclay materials.

V. Conclusions

From the preceding investigations the following conclusions may be derived:

1. Spalling fractures are caused both by shear and tension stresses.
2. Spalling which occurs on rapid heating is due entirely to shear stresses.
3. Spalling on cooling is due mainly to tension stresses and to a small extent, to shear stresses.
4. There are no large tension stresses on sudden heating.
5. The shear stresses are about equal on either heating or cooling and are about one-half the value of the maximum tension or compression stresses.
6. Shear fractures occur suddenly near the edges and corners of the solid and cracks enter the original surface on the lines of shear, that is, at about 45° to the surface. Close to the edges and the corners the fractured surface is curved slightly like the lines of shear stress.
7. Tension fractures appear across the bricks in parts remote from the corners due to concentration of tension stresses at these points. They start at the surface and penetrate deeper and deeper into the solid with each cycle of cooling. In general, the fractures follow the lines of principal stress and enter normal to the surface.
8. Fireclay bricks show plastic flow in shear at approximately the same temperature as they show deflection in a compression load test.

REQUIREMENTS OF REFRACTORIES FOR MANUFACTURED GAS PLANTS[1]

By Sandford S. Cole[2]

ABSTRACT

The requirements of the refractories used in gas producers, water gas sets, horizontal retorts, vertical retorts, and gas and coke ovens are discussed with respect to the specifications which the material must necessarily meet to prevent failure of the installations. Illustrations show various types of installations and details of certain refractory shapes employed. The temperatures encountered in various portions of the carbonizing chambers, flues, and regenerators give a fair idea as to the duty which the fire brick must meet in operation.

Introduction

The manufacture of artificial gas by heating coal to form coke has been practiced since 1802, when it was made practical by Murdock at Soho, England. Some of the original principles are still employed, but in general the by-product gas oven is replacing retorts in larger installations in this country. The production of gas by means of the gas oven is steadily increasing because of the superior grade of coke which is produced in these ovens and because of other advantages which they possess. The gas oven has been designed with the same underlying principles and general construction as the by-product coke oven used in the steel industry.

The refractories used in gas manufacture are dependent on the type of installation and the way in which it is operated. As to types of installation, there are four general classes, *viz.*, the gas producer or water gas set; the horizontal retort; the vertical retort (intermittent and continuous); and the gas oven. The general construction of these various types will not be considered in detail nor the exact method of operation described, but the requirements and service expected of the refractories will be discussed.

Water Gas Sets and Gas Producers

The water gas machine is being used today for production of about 60% of the gas manufactured for domestic consumption. In this machine, the brick are subjected to fairly high temperatures, the highest being 1300–1400°C. The brick are also subjected to changes in temperature in the reversal of air and steam, and in clinker removal. To remove the clinker, the doors at the bottom are opened and spalling

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. Received Dec.10, 1925. (Symposium on Gas House Refractories).

[2] Industrial Fellow, The Koppers Company Laboratories, Mellon Institute, Pittsburgh, Pa.

is apt to occur by the cooling effect of the outside air. The clinker is sometimes broken by quenching with water. The brick are also apt to be injured by blows from the clinker bar. Furthermore, the brick are somewhat attacked by the coal ash slag.

The brick used in the lining of the machine must be fired to a temperature which will give them a low percentage of expansion or contraction on reheating to 1410°C. The reason for this is that when set up in the shell a very close fit is effected and the brick are set so that joints are gas tight. If the brick shrank or expanded over the amount allowed for in setting the lining, either cracks would occur or else the lining would buckle due to excessive expansion. The brick must be able to withstand a load of 25 pounds per square inch to 1350°C according to the A.S.T.M. method. The brick should have a rather coarse texture, should be fairly porous, and should give a high value on the spalling test. It has been found good practice to use brick which have a fusion point of Orton cone 29, less than 5% linear shrinkage under load to 1350°C, and less than 1.5% linear shrinkage on reheating to 1410°C. The brick, "as received," should withstand at least ten dips according to the A.S.T.M. spalling test and seven dips after reheating to 1410°C. The lower the ferric oxide the better will be the resistance to carbon monoxide action. The mortar used to set up the brick should have a fusion point of Orton cone 28 and should be finely ground and evenly mixed. The blocks used in certain portions of the set occasionally offer difficulty in molding and drying, but key blocks and key brick, and 9-inch straight brick compose the largest portion of the lining.

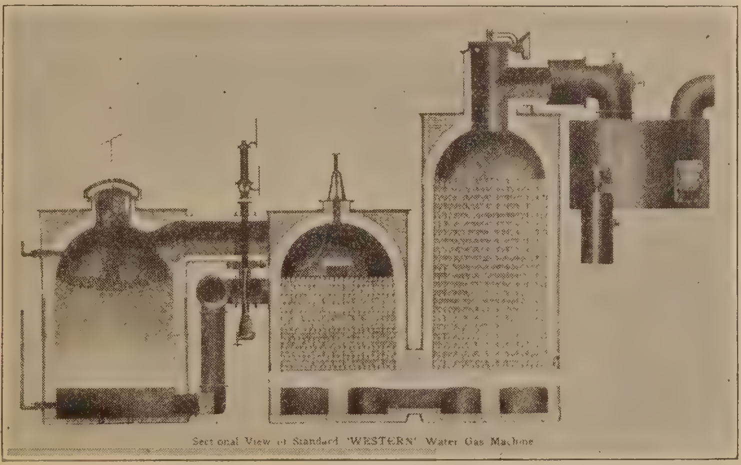

FIG. 1.—Eleven foot "Western Gas" water gas set.

In the carbureters and superheaters the brick are subjected to temperature changes which are liable to cause spalling. The temperature is generally not severe and a medium grade of brick is used for the walls and checker work. In the checker work there is a heat exchange rate to be considered and a brick which absorbs and releases heat most rapidly is desirable. The oil sprayed into the carbureter is also apt to cause spalling of the brick by the sudden change in temperature.

However, all the brick are not struck by the oil spray and therefore the entire mass of brick work is not endangered by spalling failure from this source.

The refractories used in the settings of the carbureter, superheater, and generator are usually re-pressed, soft mud brick of the same type as are used for regenerator brick in the coke ovens and open hearth steel furnaces. Extensive research has been done recently upon the use of carborundum in water gas sets. A block has been developed which has shown an improvement over former refractories and a saving in operation costs. The brick in the generator are subjected to the most severe service in the whole equipment and should have a smooth surface and be true to shape. Thus the ash and clinker attack will be reduced. Since the machine is of a definite size the brick must fit exactly and have as thin a joint as is practical.

In the straight gas producer a heavy duty brick is not required, although the refractory should give a good spalling test. In general, it may be said that the brick and shapes used in gas producers should have a fusion point above cone 27, and should stand eight or more dips on spalling test. They should be of a rather porous structure, should be fired to a temperature 100–200°F higher than will be met in the producer and should be as low as possible in Fe_2O_3 content. In the gas producer the refractory lining must be able to withstand any abrasion due to poking or stirring of the charge.

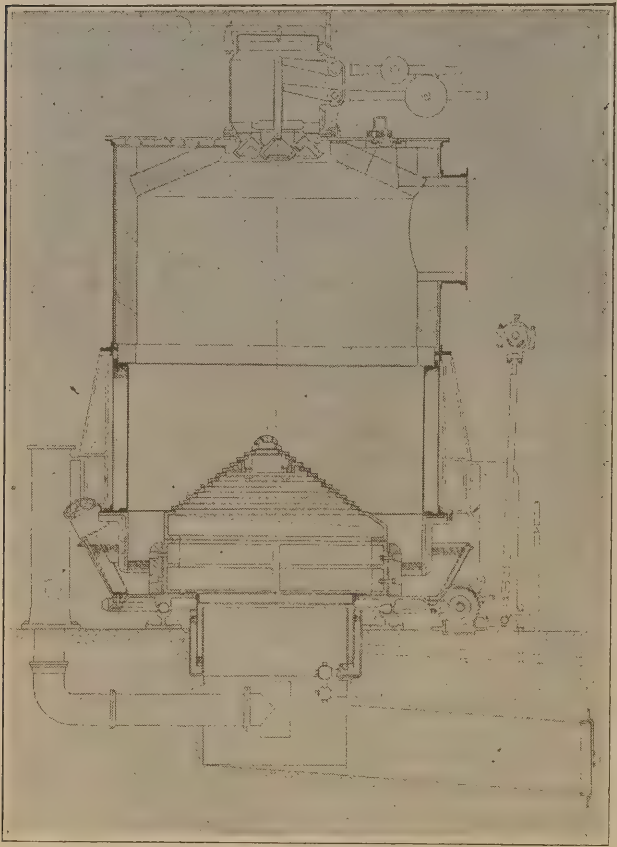

FIG. 2.—General arrangement of Koppers-Kerpely gas producer.

Horizontal Retorts

In horizontal retort practice, different problems are met and several kinds of refractory materials are required. The retorts themselves may be of several types, *viz.*, the one-piece hand molded, machine molded or cast retorts, the aluminous segmental retort, and the segmental retort with the lower half of aluminous fire clay and upper of siliceous, or silica fire brick. The general tendency of today is to use as much silica as possible in the retort. The salts in coal have a very marked corrosive action on the clay retort, and furthermore such a retort will not withstand so high a temperature as will silica. The action of ash usually does not commence until 1300°C is reached. The deposits of carbon and ash are removed by scraping or scurfing and the refractory must be able to withstand abrasion. The retorts vary in thickness but are generally from 2½ inches to 4 inches thick.

The temperature requirements of the shapes are high and the strength under load should be that of first quality brick. In England the retorts are sometimes glazed on the interior, but this has been found to be unnecessary since the carbon deposit makes the walls gas tight.

There are manufacturers of retorts in this country who wash the inside and exterior of the finished piece with a slip made of the same material as is used in the batch mix. This washing is done in order to prevent gas leakage before the walls have become carbonized. This practice is not permitted in England without the consent of the engineer in charge of construction. The carbon formation often works into small cracks in the fire brick or silica and when scraped the carbon sometimes pulls away pieces of the refractory. An example of this is shown in Fig. 3 of a piece of wall carbon. This enlarged cross-section (4×) also shows a deposit of carbon in the pores of the silica brick.

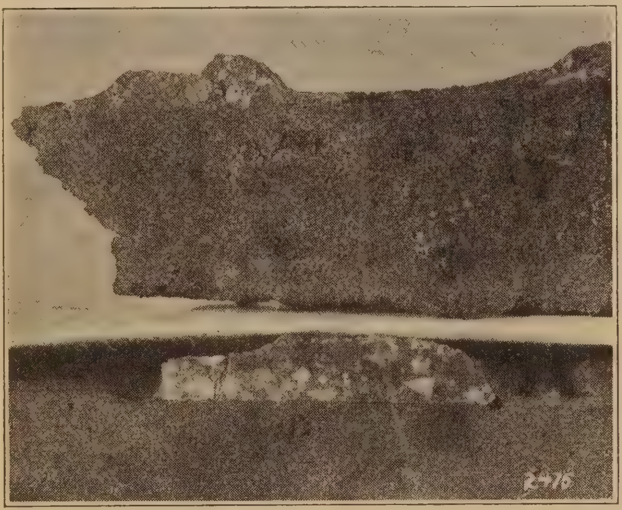

FIG. 3.—Cross-section of silica brick chip and carbon from oven wall. Enlarged 4 ×.

The aluminous retorts are usually made from a mixture of plastic fire clay, flint fire clay, and "bats." The siliceous retorts are ganister and clay mixed together, the clay serving as a bonding agent. The silica content of the mixture varies from 87–92%. All refractories should be fired to a temperature higher than will be reached in the carbonization of the coal so that there will be no excessive shrinkage or expansion. Silica retorts should be fired to a temperature of about 1450–1500°C so that a nearly complete inversion of quartz to cristobalite and tridymite will occur. The consumer should give the manufacturer a fairly clear idea of the heat duty which the refractory must meet, and by this means a manufacturer can produce fire brick which will serve the user's needs and give satisfaction.

Silica and quartzite (siliceous) brick are used to a large extent in the arch of the combustion chamber. The ability to withstand the heat under load makes the silica a very desirable material. Fireclay brick and shapes are used for the shields and supporting walls on which the retorts rest, and for the recuperator blocks.

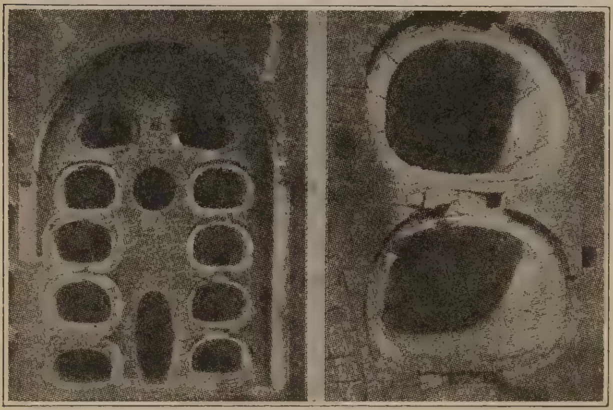

FIG. 4.—Bench of horizontal retorts having supporting walls of silica.

Figure 4 shows a setting[1] which had given 2,150 days of operation. The combustion chamber was of silica and the balance of fire clay. A setting which has over 3,000 days' life is considered to give very good service.

The retort settings are operated at a high temperature to give rapid gasification. The temperature in the combusion chamber and around the retorts is from 1300–1400°C (2372–2552°F). The molded retorts tend to crack after a comparatively short time owing to stresses and strains which are set up. Since there are no joints to relieve the strains, cracks naturally form. The segmental retorts have joints which are supposed to take up any distortion that may occur.

Vertical Retorts

Vertical retorts for the carbonization of coal are being used to some extent in this country and quite extensively in Europe. The types of refractory lining for these are undergoing a change due to the demand for the use of silica brick. England has, until recently, been using quartzite brick and fire brick of 70–85% SiO_2 for liner blocks. In the past few years the use of silica for the lining of the retort has increased. The shapes used are not so intricate to manufacture, as in the case of horizontal retorts and resemble the coke oven blocks in many respects. An advantage of the use of silica is that it can be made thinner because of its high compressive strength at high temperatures, thus permitting greater heat flow.

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[1] From an article on "Gas Retorts" in the *Gas World*, June 28, 1924, by Mr. Emery.

Engineering practice in this country always favors construction in which the flue walls and retort walls consist entirely of silica brick and shapes. The mortar used in this type of settings is a ganister, bats, and clay mixture, containing 90–93% SiO_2 and having a fusion point of cone 28 or more, with sufficient fineness to work well and enough clay to keep the bats and ganister from settling out when mixed with water. By using brick which have an apparent specific gravity of 2.40 or less, the expansion in the walls is even and not excessive at any one point.

The fusion point should be cone 31 or higher. The brick should be able to stand a load of 25 pounds per square inch to 1500°C and have not more than 2.5% permanent expansion. The shapes and brick must be within $\frac{1}{8}$ inch of the specified size and must give a good ring when struck with a hammer. They should be devoid of cracks, and true to shape.

The fireclay and quartzite settings may be attacked by salts in the coal, causing failure. In order to obtain a high throughput, the flue temperature must be fairly high. Silica, with its greater strength and resistance to salt corrosion, outlasts the other settings and permits a much more rapid carbonization. It is the usual practice to operate the vertical retorts with a temperature in the flues of 1050–1400°C. Quartzite settings cannot safely withstand the higher temperatures. Although it has been stated by some writers that such settings have been operated at 1300°C, this must be considered a maximum.

Steaming is practiced in the vertical retort, but no great difficulty is found from spalling and erosion if silica is used, although it does occur with clay and quartzite settings. The steam causes the walls to erode in the region of the steam nozzles. This action is thought by some observers to be caused by a partial chemical reaction between the constituents of the fire clay and the steam. This failure is similar to a spalling action and this is generally conceded to be the cause of the failure. When retorts of silica flue wall construction are steamed, the failure does not occur which indicates that a reaction may occur with clay. The advantages of the use of silica in the settings are:

1. Higher rate of carbonization
2. Longer life
3. Rigidity and stability at high temperatures
4. Resistance to salty coals
5. Sulphur compounds do not attack the combustion chamber

Following are British requirements for gas house refractories taken from the "Standard Specifications of Institute of Gas Engineers":

Clause 1. The retorts or retort shall be made of
(*a*) Suitably prepared raw clay and clean fired clay or "grog." "Grog" which would pass test sieve having 16 meshes to linear inch is undesirable
or (*b*) Silica or siliceous material

or (*c*) Aluminous material
or (*d*) Carborundum or other refractory material
or (*e*) Suitable mixtures of the above

Refractoriness *Clause 3.* A piece of material shall show no signs of fusion when heated in a suitable furnace to a temperature of not less than Seger cone 28 in an oxidizing atmosphere ——.

Surfaces and Textures *Clause 4.* All surfaces shall be reasonably true and free from flaws or winding; and, after firing, no "washing" shall be done without the consent of the engineer. The material shall be evenly fired throughout and contain no black core. The texture throughout shall be even and regular, containing no holes or flaws, and the apparent porosity shall be not less than 16%.

After Expansion and Contraction *Clause 5.* Test piece 2½ to 3x1½ to 2x1½ – 2 inches when heated to 1410°C and maintained at that average temperature for two hours shall not show a change of more than 1.0%. . . .

Fire Bricks, Blocks and Tiles ". . . . shall not contain more than 75% SiO_2 . . . .

Refractoriness *Clause 1.* Two grades of material are covered by this specification to be called No. 1 and No. 2 grade.

(1) Material showing no fusion when heated to a temperature of not less than Seger cone 30.
(2) . . . . to a temperature of not less than Seger cone 26.

Clause 4. . . . shall not show after expansion or contraction.

No. 1 grade—0.75%
No. 2 grade—1.15%

Variation from Measurements *Clause 5.* 9 x 4½ x 3 - inch brick shall not vary ±1.5% in length and 2.0% in width or thickness.

Silica Brick, Blocks, and Tiles Materials covered by this specification are divided into two classes.

(1) . . . . 92% or more of SiO_2 is known as "silica" material
(2) . . . . 80–92% of SiO_2 is known as "siliceous" material

Refractoriness Silica material—not less than Seger cone 31
Siliceous material—not less than Seger cone 29

Expansion or Contraction . . . . when heated to 1410°C and maintained for two hours shall not show after expansion or contraction of more than 0.5%.

. . . . same allowance in variation of measurements.

The process of manufacture, the fabrication and clay mixtures are entirely a matter of experiment left to the producer of the ware. The material must be fairly coarse in grind to prevent spalling and be well fired. The compounding of batches of clay which will give a good grade of refractory for retort setting is a matter of experience and knowledge of the industry. The action of coal and coke on the lining and the temperature duty to which it will be subjected is obtained only by experimental work. A study of the action of the ash from the producer is fairly essential and a means of cleaning gas before use eliminates this trouble.

Vertical retorts have recently been developed, particularly by The Koppers Company, to a capacity and efficiency comparing very favorably to some of the gas ovens which will be discussed below. The refractories for such verticals have substantially the same requirements as for such gas ovens.

By-Product Gas Oven

Gas for domestic consumption is now produced to a very large extent by the by-product gas oven of the same type as the by-product coke oven which has performed so successfully in the steel industry. More than 60% of the coal gas sold in the United States is derived from by-product coke or gas ovens (exclusive of that used by the steel industry).

These ovens are built in two sizes, *viz.*, the large oven of the same size as used in the steel industry, constructed for production of gas and coke in large cities; and the small gas oven built on the same principle and design as the large oven, but differing in length which is about half that of the large oven. Over 90% of the by-product coke and gas ovens installed for gas companies in the United States during the past three years have been of the Becker type, constructed by The Koppers Company, Pittsburgh, Pa.

These ovens are constructed entirely of silica from the base of the regenerators to the top of the cross-over flues. The superiority of silica has long been shown in the by-product coke oven, where it has been used since the first installation of Koppers ovens at Joliet in 1909. In the construction of the oven several shapes are used which are made by the hand-molded process, well known to the refractory manufacturer. The silica brick and shapes are tested to see that they meet with all requirements. The silica being able to withstand high temperature service permits the flues to reach 1500°C without danger of failure.

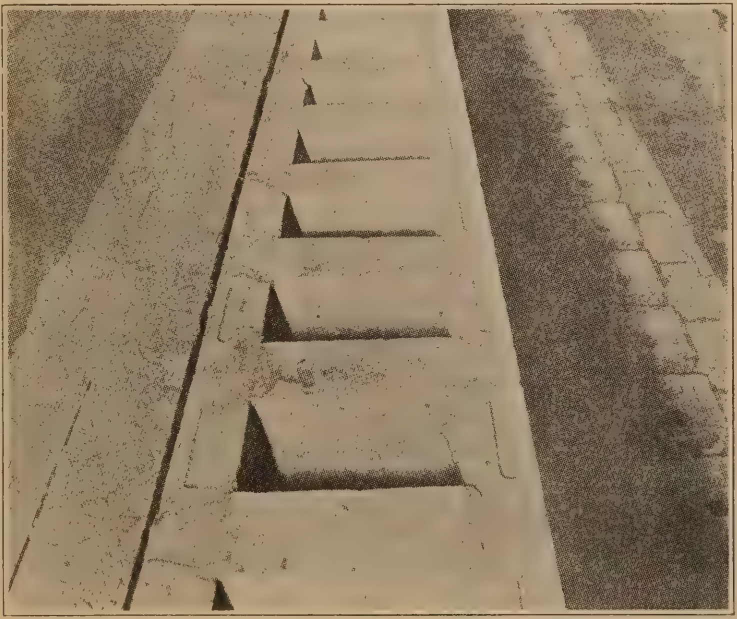

FIG. 5.—Rectangular flued coke oven in process of construction.

Figure 5 shows an oven in construction. The flues and oven proper are shown in the photograph.

The silica walls are not subjected to abrasion, since the coal contracts slightly on coking, thus leaving the wall clear. There is, however, an abrasive action on the floor at the time of pushing. Fireclay blocks are used here, giving good service and causing no great difficulty from abrasion. The silica wall is occasionally subjected to a rather rough treatment when the coke sticks in the oven and, in endeavoring to remove the coke, the implements used often strike the walls. Care must be taken when the ovens are started to be sure that the silica is not heated too fast, which would cause strains due to too rapid expansion and cause cracks to form.

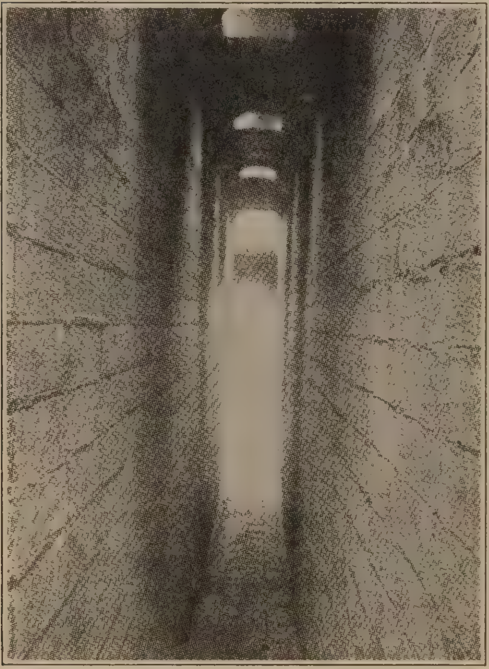

FIG 6.—Quartzite and silica coke oven walls before use.

An illustration of the action of salts upon quartzite and of the resistance of silica is shown by Figs. 6 and 7.[1] Figure 6 shows two walls of a coke oven, the left being made of silica and the right of quartzite. Figure 7 shows the same walls after use. The action of salt corrosion is quite noticeable in the quartzite shown on the right.

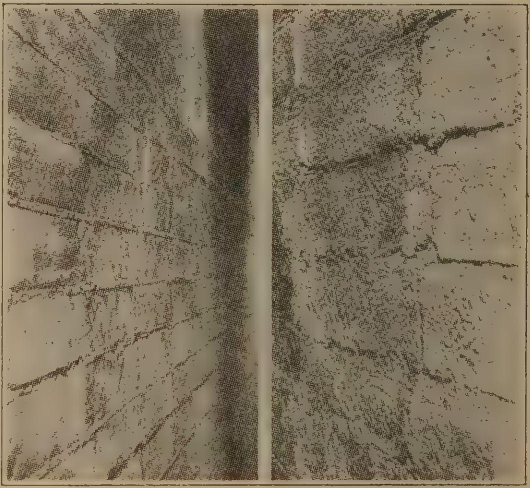

FIG. 7.—Quartzite and silica coke oven walls after use showing effect of salty coal on refractory.

The shapes used in the flue and wall construction are designed so that a gas tight joint is effected and the maximum strength in wall structure is produced. This joint is further improved as soon as the silica has been filled on the surface with a thin layer of carbon. This carbon is formed by the cracking of the gases and tars produced by the distillation of the coal. Silica which has been in use continuously for twelve years has been studied and seems to be unaffected by this long service. There is a slight formation of silica glass on the flue side and an apparent, complete inversion of the quartz to tridymite and cristobalite. There is a slight infusion on the coke side of iron from the coal ash, giving a discoloration to the piece. This color also might be from the cracking of the ferrocarbonyls that are sometimes formed in the gas.

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[1] The photographs are from Heinrich Koppers' "Mitteilungen" Jan. 1921, pp. 24 and 25.

In most by-product ovens the prevailing practice is the use of regenerators where fire brick are set unmortared in a cross-hatch manner, giving as great a surface exposure as possible. It is desirous to have as many brick in the regenerator as practical and yet have a large surface exposed so that the hot or cold gases, whichever may be the case, will give up or receive heat more readily. The brick which have a high heat absorption value are the most desirous. The brick must have a fairly high fusion point although the temperature in the regenerator seldom goes above 1250°C. The regenerator brick are subjected to air spalling because, upon reversal, cold air is drawn into the base and heated on passing up through the regenerator. When producer gas is used for heating the oven, the regenerator is divided into two sections. One is for preheating the producer gas and the other for air. The air first passes over the bricks which are of the lowest temperature, and the air gradually increases in temperature as it rises to the top of the regenerator. This rise in temperature, at nearly the same rate as that of the bricks in the regenerator, has a beneficial effect upon the life of the fire brick. The hottest brick are not struck by cold air, but by air or gas which has been preheated to a temperature a little lower than that of the brick.

Insulation

The use of an insulating material forms an important part of oven and retort construction. By the decrease in heat losses the efficiency of the installation is increased to quite an extent. The heat formerly lost by radiation and convection is saved and gas consumed in carbonization of the coal is cut down in a direct proportion. This gives a greater amount of gas for disposal and the cooler battery also makes working conditions much better for men employed. The materials found to give the best results are diatomaceous earth and a brick of a porous, non-conductive nature. The diatomaceous earth is used in both a powdered condition and in brick form.

Inspection and Testing

The question of inspection and testing of the refractories used in gas house installations is a vital one. The success of a battery depends a great deal upon the quality of refractory used. The testing of each car of material shipped gives a fairly close check upon brick supplied to the consumer. When the consumer states clearly in his specification the tests which the brick must withstand the producer is able to furnish a grade of refractory which proves quite satisfactory. The testing of fire brick, silica brick and the mortars used for setting the brick has proved to be of value in many ways. The Koppers Company, by close checking of the brick supplied for oven construction, have not had a single failure due to the refractories employed. In the testing of the

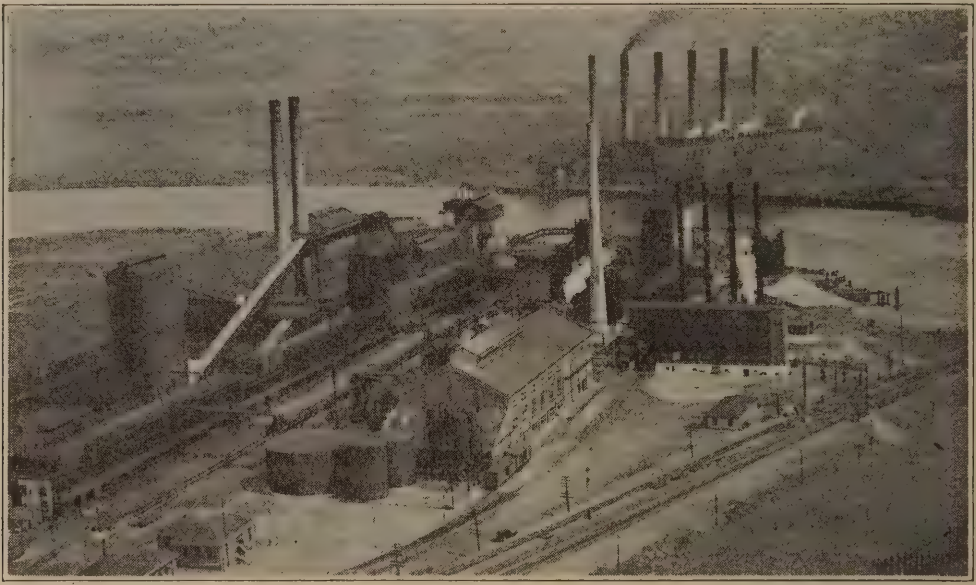

FIG. 8.—View of Seaboard By-Product Coke Company's plant at Jersey City, N. J.

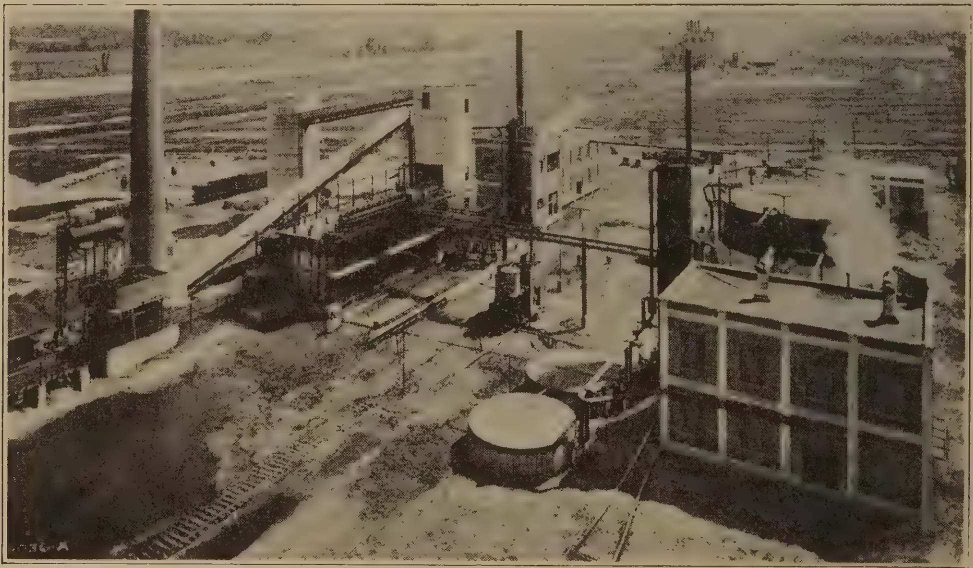

FIG. 9.—View of Consumers Power Company's plant at Zilwaukee, Mich.

materials many facts have been discovered which have led to an improvement in these materials. The close coöperation between the consumer and producer proves to be beneficial to both parties concerned. The consumer gets satisfactory brick and the manufacturer a satisfied customer.

The tests carried out upon silica and fire brick are made according to A.S.T.M. methods. By this system, a common means of comparison of each sample submitted is afforded and the results upon all samples tested may be compared from year to year, giving a valuable piece of information relative to the variation in materials used. These tests are well known to the firebrick manufacturer and to most of the consumers of refractories so that it will not be necessary to describe them.

Silica brick should be tested for apparent specific gravity, per cent porosity, fusion, and the load test of 25 lb. per sq. in. to 1500°C. The fire brick should be tested for fusion, per cent porosity, load test of 25 lb. per sq. in. to 1350°C, spalling, and reheating to 1410°C. Other tests may be carried out upon the brick as is deemed advisable from time to time. The silica and fireclay mortars should be tested for screen analysis and fusion.

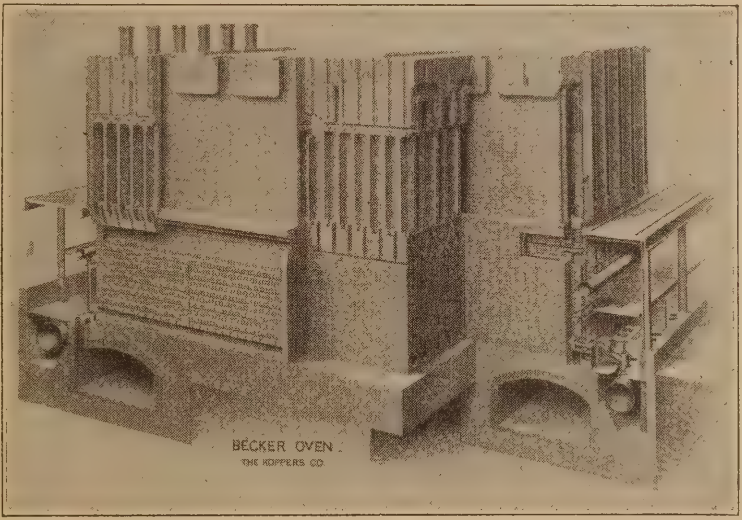

Fig. 10.—Model of the Becker oven.

The two photographs showing two installations of Koppers ovens are: first, the plant of the Seaboard By-Product Coke Company at Jersey City, N. J., (Fig. 8), consisting of 165 Koppers ovens which supplies about 25,000,000 cu. ft. of gas per day for domestic consumption. The other is the plant of the Consumers Power Company at Zilwaukee, Michigan, (Fig. 9) which consists of 19 small Becker gas ovens, supplying 2,350,000 cu. ft. of gas per day for domestic consumption.

Figure 10 shows a model of the Becker Oven.

A PHENOMENAL CASE OF TILE BREAKAGE[1]

By R. A. Hart[2]

ABSTRACT

In 1921 an interesting case of tile breakage was discovered at Hinckley, Utah, in a drain which had been laid for three years, the backfill ranging from 2 to 6 feet. The breakage was inversely proportional to the depth of the backfill and the tile had broken upward, all conditions of fracture being reversed. Some of the tile did not break until a portion of the backfill was removed. Investigation showed that the tile had been laid in a trench but slightly wider than the outside diameter of the tile, the material being a highly colloidal clay, extremely dry. The line was for relief of another drain and no water entered the line until the latter was tapped. Water percolating through the joints and saturating the adjacent clay caused an expansion which crushed the tile laterally. Subsequent laboratory studies showed the clay to have a coefficient of expansion of 178.5.

When an investigation is made of the crushing strength of a piece of drain tile, the sample is tested to destruction.

The test piece is laid on its side, supported either on two strips or on a bed of sand fitted to the lower quadrant of the tile and pressure is applied to the upper part of the tile either through a strip laid along the middle line of the crown or a piece of hose partly filled with water placed in the same manner, or through a sand bed fitted to the upper quadrant of the test piece. In any case the pressure is directly downward and is uniformly distributed throughout the length of the test piece. The tile is not supported at the sides.

The deformation before actual breakage is very slight and when crushing strength is exceeded by the applied pressure, the specimen breaks into four parts along planes passing through the horizontal and vertical diameters of the tile. The two lower quadrants fall apart while the two upper quadrants fall concave sides downward, upon the two lower quadrants.

The load may be regarded as being applied along the middle line of the upper half of the test piece and there is a tendency, therefore, for a downward movement along a plane passing through this line. This tends to produce shear along the plane and a bending moment along a plane intersecting the walls along the horizontal diameter. Compression is set up in the upper half of the wall at the top, in the inner half of the walls at the sides, and in the lower half of the wall at the bottom. Tension is produced in the lower half of the wall at the top, in the outer half of the walls at the sides, and in the upper half of the wall at the bottom.

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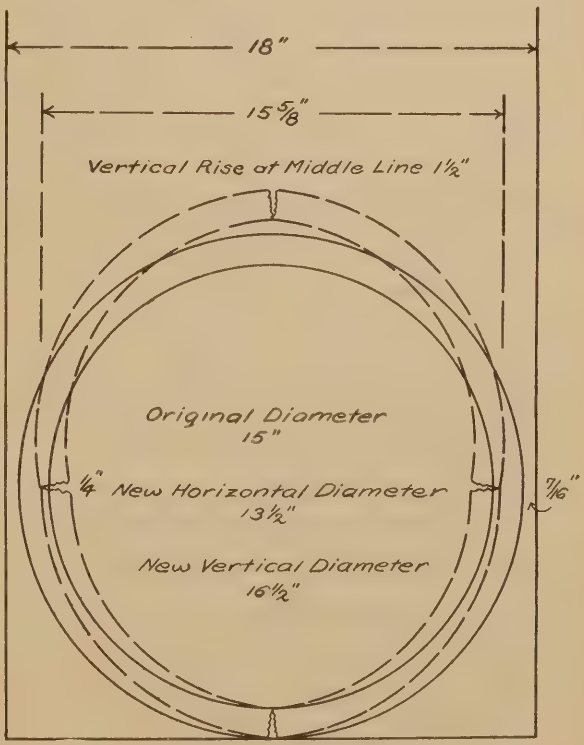
[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Heavy Clay Products Division.) Received April 3, 1926.

[2] Secretary-Manager, Western Clay Products Association, Salt Lake City, Utah.

In the field, tile are supported by the bottom of the trench in which they are laid. The pressure is that produced by the backfill and any superinduced loads. It is distributed over the upper half of the tile. The sides are supported by the backfill. Breakage of tile under field conditions is frequent, but collapse of the tile is rare. For this reason the breakage is often unnoted. It is usually indicated by depressions in the backfilled trench or by the direct inflow of surface water and in some cases by the development of well defined openings in the backfill from the tile line to the ground surface.

When a tile, broken under field conditions, is uncovered, it is usually found to have broken into four parts, as in a laboratory test, but, unless actual collapse has taken place, the conduit will still be intact but deformed. The vertical diameter will be found to have decreased and the horizontal diameter to have increased, while the four quadrants of the tile will be found to have separated considerably at the inner edge of the wall at the top and bottom and at the outer edge of the walls at the sides; that is to say, wherever the tension was maximum.

Breakage Due to Expansion of Soil


18"
15 5/8"
Vertical Rise at Middle Line 1½"
Original Diameter 15"
¼"
New Horizontal Diameter 13½"
7/16"
New Vertical Diameter 16½"

A CRUSHING OF TILE BY SIDE PRESSURE

Fig. 1.

An interesting case of tile failure was discovered in Millard County, Drainage District No. 1, near Hinckley, Utah, in the spring of 1921. A large number of lengths of 15-inch tile were found to have collapsed under backfill ranging from two to six feet. The collapse was not discovered until an attempt was made to remove the tile for replacement in another locality. The tile had been in the ground for three years. Where the backfill had a depth of six feet the tile had not collapsed and there was a very small percentage of breakage and the fractures were normal. But strangely enough, where the backfill ranged from two to three feet, the breakage was 100%, and many of the tile had collapsed. Examination disclosed the fact that the tile had broken *upward* and were badly deformed, the vertical diameter being 16$\frac{1}{2}$

inches, while the horizontal diameter was only $13\frac{1}{2}$ inches, the cracks being open as much as $\frac{1}{4}$ inch wherever the wall was in tension, which was at the usual positions of compression. Fig. 1 illustrates the deformation.

Where the backfill was somewhat greater, breakage did not occur until a portion of the backfill was removed, notwithstanding the fact that the tile had been laid three years. The workmen could hear distinctly the report as the tile broke.

The tile had an outside diameter of $17\frac{1}{8}$ inches and were laid in a trench 18 inches wide. The material was clay and was dry when the tile were installed, the drain being a relief line, tapping an overloaded main drain within the district.

Being laid in dry soil, water was lost through the joints of the tile and the surrounding material was saturated, causing an expansion of the clay. This expansion was sufficient to reduce the width of the trench from 18 to $15\frac{5}{8}$ inches and to produce great side pressure on the tile.

Where the depth of backfill was only two to three feet the transmitted pressure was sufficient to lift the backfill, thus permitting the deformation and collapse of the tile. With greater depth, the pressure was not sufficient to lift the weight of the backfill, but, on partial removal of the backfill, collapse occurred.

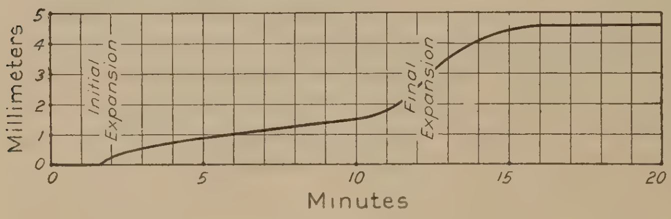


FIG. 2.

The dry clay was found by A. E. Vinson to have an expansion on wetting as high as that for any soil examined. The soil has a double expansion, as in Fig. 2. When placed in water a rather slow initial expansion took place. This would serve to firm the backfill of a trench and bring the soil tight around the tile. The second swelling is much more sudden and something would have to give way. With the soil packed by the first swelling, the pressure produced by the second swelling would be ample to crush tile. An attempt is now being made actually to measure the unit pressure produced by the expansion.

AN ATTEMPT TO SECURE A UNIFORM MIXTURE OF FINE AND COURSE PARTICLES IN GROG FROM A BIN[1]

By W. A. Hull

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ABSTRACT

A sloping chute or trough down which the stream of grog flows to the bottom of the bin, instead of dropping with a free fall places grog in bin in such a way that it comes out of the bin fairly well averaged as to sizing.

It is a matter of common observation that ground grog, discharged into a bin in a more or less continuous stream, as by an elevator or conveyor has a tendency to become classified in point of fineness, in such a way that when the material is drawn out of the bin, what is drawn out at one time will be mostly fines and at another time mostly coarse. Many manufacturers have had this tendency to contend with. Some have overcome it in one way and some in another and very probably others are still putting up with it. It is not the purpose of this paper to review or discuss the various ways in which the matter has been taken care of, but simply to tell what has been done about it in one place in the hope that some one may gain from this attempt an idea that may be useful in solving his own problem.

The Midland Terra Cotta Company has one large bin for terra cotta grog and another large bin for ground clay. It is the practice to grind clay and grog separately and to pug a mixture from these two bins. Due to the shape of the grog bin and the fact that the discharge from the screen is directly over the opening to the chute by which the bin is emptied the conditions were favorable for getting all varieties of size combinations in the grog. The condition had been overcome, to some extent, by means of a stack of inverted wooden V-shaped troughs, so built up that the grog in passing down through the stack was considerably retarded. It was finally decided that the most promising simple means would be to put some sort of a chute across the bin from top to bottom, so that the grog, instead of dropping from a considerable height and scattering out, would start piling up at the bottom of the chute when the bin was empty, and form a pile that would gradually work up the chute so that at no stage would it have any free drop.

The first chute installed was not steep enough and the grog accumulated in the lower part of the chute, blocking it so that the stream flowed over the side, well up toward the top. But the chute was hinged near the top so the angle of the lower part could be changed. It was possible to find about how steep it had to be in order to operate properly

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Terra Cotta Division.) Received April 28, 1926.

when the grog was somewhat moist and consequently had the greatest tendency to bank up. After this was determined, a more permanent chute was put in.

The grog was already extensively classified before it even got into the chute and the stream, flowing down the chute, was stratified. This condition could be remedied, to some extent, by baffles or obstructions but there was a strong tendency for the grog, in motion, to separate again.

In a constantly flowing stream, fine and coarse particles are constantly arriving at the bottom of the chute and if they would accumulate there for a short interval, instead of going their separate ways, the accumulation would be an average mixture of coarse and fines. If this accumulation would flow down the side of the pile the material would stay mixed, clear to the bottom of the pile. As a matter of fact, something approaching this does occur.

If the grog were always of the same moisture content so that it would always flow the same, this action would be closely approximated. If the chute be steep enough so that the grog will not bank up in it too much and overflow too high up when the grog is damp, then it will not bank up enough when the grog is dry. With a chute as steep as it has to be for all conditions, the damp grog behaves best. Drier grog has more of a tendency to keep moving and there is a tendency for the finer portion of the stream from the bottom of the chute to curl around and flow backward under the chute, and the upper, coarser part to flow out over the top of the pile and make its way out toward the edges. Even so, the separation is not anything like what occurs when the grog has a free fall.

With the material dropping from the discharge end of a chute located almost directly over the hole in the bottom of the bin through which it would be drawn out, the fines would accumulate over this hole during the entire process of filling the bin with the result that during the emptying what was taken out first would be mostly fines, what came out last would be mostly coarse, and what came out between times would vary from fine to coarse. With a long chute extending down into the bin and across it, the pile starts at a point far removed from the opening in the bottom of the bin and as the bin fills up the top of the pile gradually travels across the bin toward a point almost directly over the hole in the bottom. The result is that although the material in the bin is not entirely homogeneous the finer and coarser portions are so distributed that when the bin is emptied, the slides on the surface of the crater, which forms in the emptying process, catch some of the fines and some of the coarse at every stage of the emptying and give a tolerably good average.

According to screen analyses of samples taken at different stages of the emptying, the results are good. It cannot be said, however, that enough samples have been tested to make sure that the material may not fail to average properly at times. For practical purposes the pressing shop is a reasonably reliable source of information and so far, over a period of several months, the reports have been satisfactory.

It seems to the writer, after studying the flow of grog in this particular bin that, in the case of a deep bin of small cross-section, a spiral chute might be good. It was found that by placing a temporary stop in the chute, near the top, so as to hold back a small accumulation of grog and then releasing, so that the grog would go down the chute intermittently instead of in a continuous stream, an effect was produced which would give less separation than took place with a continuous stream. It is thought that a hinged gate, properly counterweighted, could be adjusted to a chute in such a way that when a sufficient quantity of grog had accumulated, the gate would be opened by the pressure and the intermittent delivery would be automatic. In our case this does not seem to be necessary because of the averaging which takes place in emptying.

Midland Terra Cotta Co.
Cicero, Illinois

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SOME FACTORS INFLUENCING THE RATE OF PICKLING OF SHEET IRON[1]

By J. E. Hansen and G. S. Lindsey[2]

ABSTRACT

Experiments with regard to various factors entering into pickling of sheet iron show that: (1) a freshly made sulphuric acid pickling bath pickles faster than a bath in which there is any concentration of ferrous sulphate and that (2) there is no evident advantage in adding a portion of old pickling solution to a new pickling solution "to get it to work right," although practical experience indicates otherwise; (3) increased ferrous chloride concentration in a muriatic acid pickling bath increases the rate of pickling; (4) ferric sulphate in a sulphuric acid bath will accelerate the rate of pickling, but will soon change to ferrous sulphate and then retard the rate; (5) decrease in acidity from usual strength decreases rate of pickling; (6) increase of temperature of bath accelerates rate of pickling; (7) iron annealed just previous to pickling loses 250–400% more in pickling than unannealed iron; (8) use of monel metal basket accelerates the rate of pickling due to electrochemical reactions; and (9) use of muriatic acid or sodium chloride in mixtures with sulphuric acid retards the rate of pickling.

Introduction

This is a study of the effect on the rate of pickling of the varying factors which may and do exist in the acid bath in which sheet iron is pickled.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Enamel Division.)

[2] Industrial Fellows, Mellon Institute of Industrial Research, Univ. of Pittsburgh, Pittsburgh, Pa.

In either a muriatic or sulphuric acid pickling bath the concentration of acid and the temperature of the bath may be varied at will, and with use there develops an increasing concentration of iron salts. These three variables, together with the condition of the metal itself and other external factors affecting the pickling process have been given consideration in this work.

Method of Procedure

Test pieces of 22-gage Armco Iron, 1 inch wide and 6 inches long, in duplicate, were used in this work. Glass beakers containing two liters of pickling solution were the pickling tanks, and these were placed in a thermostatically controlled water bath to insure even heating and a constancy of temperature of ±2°F during the experiment. The ratio of amount of acid present against area of iron exposed to be pickled was large enough to insure but little diminution of acid strength during the pickling time.

The loss of weight of the various samples was considered indicative of the rate of pickling or rate of attack of acid on the iron. All samples of iron were weighed before and after annealing (if annealed), and, after each pickling, were washed in water, alcohol, and ether, then dried and weighed.

Acid strength and iron concentration of each pickling bath was determined by titration with standard sodium hydroxide and permanganate solutions. Results in grams strength per 100 cc. of solution are referred to in the data as per cent by volume.

Iron in solution in the pickling acid was calculated as per cent of iron, and not as per cent of ferrous sulphate or ferrous chloride, as the case might be.

The majority of all data on pickling with sulphuric acid were determined at 130°F, which may be somewhat lower than most commercial practice, but this was the most practical temperature at which to run the constant temperature bath over a long period of time.

TABLE I

ANNEALED SHEETS

Dissolved iron in bath (%)	Gain in annealing	Loss initial 7½ min. period (gms.)	Total loss in 15 min. period (gms.)	Total loss in 30 min. period (gms.)	Total loss in 60 min. period (gms.)	Loss 7½–15 min. period (gms.)	Loss 7½–30 min. period (gms.)	Loss 7½–60 min. period (gms.)
0.0	.0187	.1550	.1620	.1682	.1790	.0070	.0130	.0240
5.16	.0205	.1775	.1825	.1880	.1990	.0050	.0105	.0215
8.18	.0195	.1195	.1245	.1295	.1385	.0050	.0100	.0190
16.40	.0210	.1365	.1385	.1430	.1500	.0020	.0065	.0135

Experimental Data

The first experiment was with sheets annealed at 1300°F for one and one-half minutes and pickled at 130°F in 6.1% sulphuric acid baths of various concentrations of iron sulphate.

The average loss in grams per sample is shown in Table I, and in Fig. 1.

The loss during the initial pickling time of 7½ minutes varies over quite a wide range, but this is due not so much to the concentration of chemicals in the bath as to the varying amount of scale of iron oxide formed on the sheets during the annealing process. The curves in Fig. 1 fall in no regular order, due to this varying amount of scale on the samples, and the relative slope of the curves through the remaining pickling intervals is hard to interpret. However, in plotting the loss in weight of samples after the original 7½ minutes pickling time (see lower portion of Fig. 1) the curves arrange themselves in a regular order, clearly indicating that with increasing percentage of iron in the bath, the attack of acid on the metal is lessened.

Since the whole curve starting from zero minutes is hard to interpret, and since the curve starting at 7½ minutes indicates the effect of the variable factor, only the latter or interpretable portion of the data will hereafter be plotted.

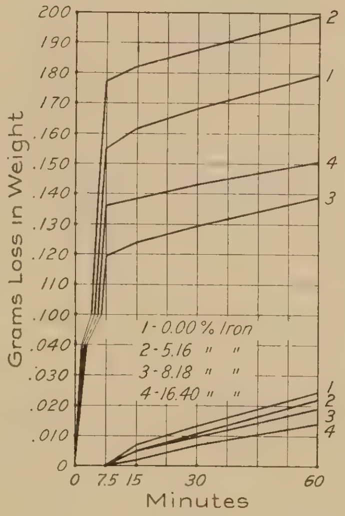

FIG. 1.—Shows actual grams loss in weight of annealed sheets pickled in 6.1% sulphuric acid at 130°F. Lower set of curves shows loss in weight after initial 7½ min. pickling period, and therefore shows relative effects of different iron concentrations of bath.

I. Effect of Ferrous Sulphate

Table II and Fig. 2 show the effect of increasing concentration of dissolved iron in the bath, and indicate the relative rates of attack of the pickling solutions on both annealed and unannealed sheets, pickled in 6.1% sulphuric acid at 130°F.

TABLE II

	Unannealed			Annealed		
Dissolved iron in bath (%)	Loss 7½–15 min. period (gms.)	Total loss 7½–30 min. period (gms.)	Total loss 7½–60 min. period (gms.)	Loss 7½–15 min. period (gms.)	Total loss 7½–30 min. period (gms.)	Total loss 7½–60 min. period (gms.)
0.0	.0080	.0232	.0485	.0070	.0130	.0240
5.16	.0065	.0185	.0390	.0050	.0105	.0215
8.18	.0050	.0160	.0350	.0050	.0100	.0190
16.40	.0045	.0140	.0305	.0020	.0065	.0135

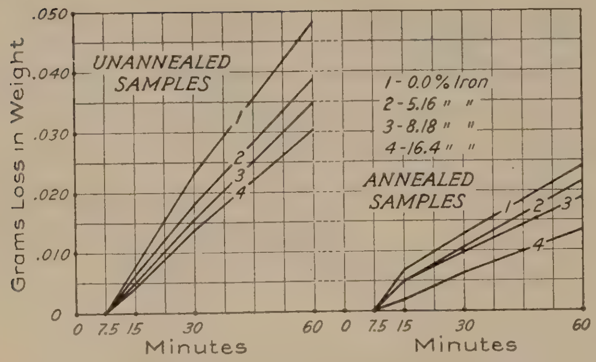

FIG. 2.—Shows relative loss in weight of samples pickled in 6.1% sulphuric acid at 130°F, varying the amount of dissolved iron in the bath.

These curves show that with increasing iron concentration in the bath (acidity and temperature constant) there is a progressive decrease in the loss of weight or in the rate of pickling of the metal.

The action of the acid on the metal during the 7½-minute to 60-minute period is less in the case of annealed iron than in the case of unannealed iron, indicating that there is less danger of overpickling the former.

There is no great difference in the slope of these curves to indicate any certain concentration of iron salt in the bath above which pickling action is slowed down to a marked degree, but by referring to the curves for unannealed sheets it can be noted that when 8.18% dissolved iron is present the rate of pickling is 28% less than with no iron present, and with 16.4% dissolved iron present the pickling rate is 37% less than with no iron present.

II. Effect of Addition of Old Pickle Solution to Fresh Acid

Since it is the practice in some pickling departments to add a portion of old pickle solution to a fresh tank of acid to "get it to work right," one part of old pickling solution analyzing 9.644% ferrous iron, 0.133% ferric iron, and 6.1% sulphuric acid was added to 4 parts of fresh 6.1% sulphuric acid pickling solution.

This results in a 6.1% sulphuric acid bath, containing 1.93% ferrous iron and 0.027% ferric iron.

The rate of pickling in this bath, at 130°F, is shown in Table III and Fig. 3.

TABLE III

	Unannealed			Annealed		
Solution	Loss 7½–15 min. period (gms.)	Loss 7½–30 min. period (gms.)	Loss 7½–60 min. period (gms.)	Loss 7½–15 min. period (gms.)	Loss 7½–30 min. period (gms.)	Loss 7½–60 min. period (gms.)
Fresh acid	.0080	.0232	.0485	.0070	.0130	.0240
Fresh acid plus 20% old pickle solution	.0060	.0195	.0405	.0070	.0130	.0255

The data indicate the lessened rate of pickling of unannealed sheets, and approximately the same rate of pickling of annealed sheets when old pickle solution is added to the fresh acid, as compared to the action of the fresh acid itself.

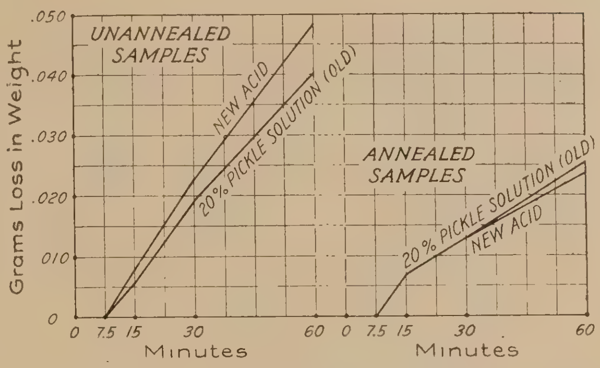

Fig. 3.—Shows effect of adding 20% of old sulphuric acid pickle solution to new pickling bath of sulphuric acid. Samples pickled at 130°F.

To determine what effect the ferric or oxidized iron salts of the old pickle solution might have on the activity of the pickling bath, ferric sulphate equivalent to a concentration of 0.4% ferric iron was added to a 6.1% fresh sulphuric acid bath and sheets were pickled at 130°F, with results as shown in Table IV and Fig. 4.

Table IV

Solution (%)	Unannealed			Annealed		
	Loss 7½–15 min. period (gms.)	Loss 7½–30 min. period (gms.)	Loss 7½–60 min. period (gms.)	Loss 7½–15 min. period (gms.)	Loss 7½–30 min. period (gms.)	Loss 7½–60 min. period (gms.)
6.1 sulphuric acid plus 0.4 ferric iron	.0255	.060	.123	.0135	.0475	.1035
6.1 sulphuric acid	.0080	.0232	.0485	.0070	.0130	.0240

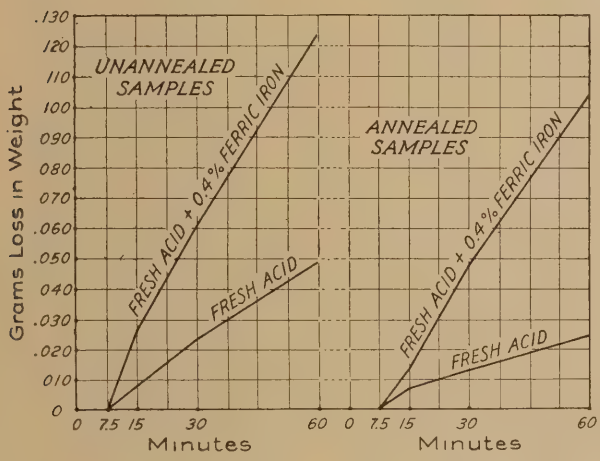

Fig. 4.—Shows effect of ferric iron dissolved in sulphuric acid pickling bath.

These curves demonstrate the accelerating effect of ferric iron in the pickle solution, which is in line with the already known corroding effects of ferric salts. The curves are presented merely as a matter of interest, because ferric salts have little to do with present day pickling practice, since they are reduced to ferrous salts by the nascent hydrogen generated in the pickling operation and would hence exist for only a short time after addition.

III. Effect of Variation in Acid Strength

A lowering in strength of acid shows a decrease in the rate of pickling, as would be expected. The relative decrease is shown in Table V and Fig. 5, using sulphuric acid at 130°F.

TABLE V

Strength sulphuric acid	Unannealed Grams loss 7½–15 min. period	Grams loss 7½–30 min. period	Grams loss 7½–60 min. period	Annealed Grams loss 7½–15 min. period	Grams loss 7½–30 min. period	Grams loss 7½–60 min. period
4.60%	.0085	.0220	.0430	.0050	.0120	.0185
5.55%	.0085	.0255	.0525	.0055	.0130	.0195
6.54%	.0095	.0290	.0555	.0065	.0155	.0265

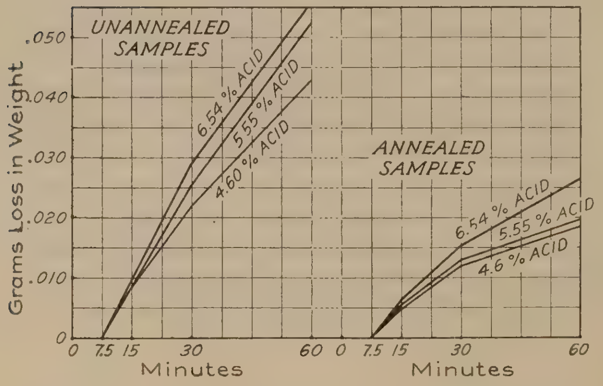

FIG. 5.—Shows relative pickling loss at 130°F, using different strengths of sulphuric acid.

This decrease in the rate of pickling due to lessening acid concentration is not, however, of as much effect as change in pickling temperature, as will be shown below.

IV. Effect of Temperature of Acid

To determine the relative effect of difference in temperature upon the rate of pickling, four trials were run, using fresh 6.1% sulphuric acid at 130°F, 150°F, 170°F, and at 190°F. The results of these trials are shown in Table VI and Fig. 6.

TABLE VI

Temperature °F	Unannealed Loss 7½–15 min. period (gms.)	Loss 7½–30 min. period (gms.)	Loss 7½–60 min. period (gms.)	Annealed Loss 7½–15 min. period (gms.)	Loss 7½–30 min. period (gms.)	Loss 7½–60 min. period (gms.)
130	.0080	.0232	.0485	.0070	.0130	.0240
150	.0110	.0350	.0740	.0105	.0250	.0500
170	.0205	.0590	.1670	.0165	.0380	.0840
190	.0320	.0930	.2355	.0275	.0745	.1975

It is interesting to note in these curves the rapid rise in the rate of pickling due to increase in temperature of the solution, and by comparison with the curves in Fig. 5 it will be noted that an increase in the temperature of 20°F will more than compensate for a 2% decrease in acidity of the solution. This fact is, of course, made use of in "killing" a pickling solution before draining the tank.

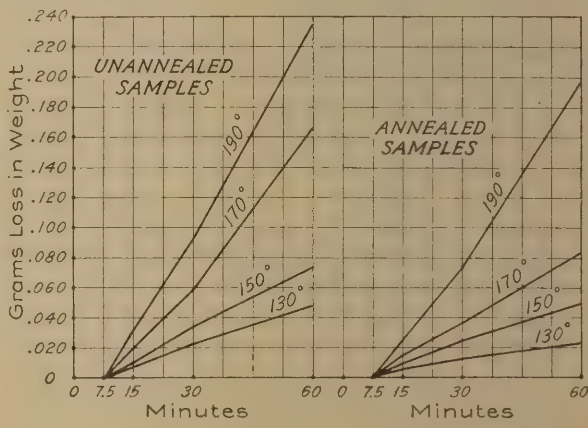

FIG. 6.—Shows relative pickling loss, using fresh 6.1% sulphuric acid at different temperatures.

V. Effect of Dissolved Iron (Ferrous Chloride) in Muriatic Acid

Changing from sulphuric acid to muriatic acid, we used a pickling solution of one part 20°Bé muriatic acid and two parts of water at 85°F (approximately room temperature). This acid analyzed 11.45% hydrochloric acid (114.5 grams HCl per liter), and with increasing ferrous iron concentration in the bath (acidity and temperature constant) we find that the rate of pickling increases, as is shown in Table VII and Fig. 7.

TABLE VII

Ferrous iron content of 11.45% muriatic acid solution (%)	Unannealed Loss 15–30 min. period (gms.)	Unannealed Loss 15–60 min. period (gms.)	Annealed Loss 15–30 min. period (gms.)	Annealed Loss 15–60 min. period (gms.)
0.00	.0040	.0100	.0050	.0090
2.80	.0050	.0135	.0045	.0125
5.29	.0065	.0155	.0060	.0150
7.57	.0060	.0155	.0055	.0140
10.24	.0075	.0235	.0085	.0175
12.40	.0120	.0275	.0105	.0220
15.26	.0140	.0390	.0110	.0275
18.84	.0130	.0365	.0130	.0330

TABLE VIII

6.1% sulphuric acid, 130°F		11.45% muriatic acid, 85°F	
Iron in soln. (%)	Loss, 45 min. pickling (gms.)	Iron in soln. (%)	Loss, 45 min. pickling (gms.)
0.00	.0405	0.00	.0100
0.45	.0330	2.80	.0135
1.05	.0295	5.29	.0155
2.04	.0305	7.57	.0155
5.16	.0325	10.24	.0235
8.18	.0300	12.40	.0275
12.55	.0245	15.26	.0390
16.40	.0260	18.84	.0365

In this case, using cold muriatic acid, we used an initial pickling period of 15 minutes to remove the varying amount of scale on each sample sheet, and based our conclusions on the rate of pickling during the succeeding pickling intervals up to one hour.

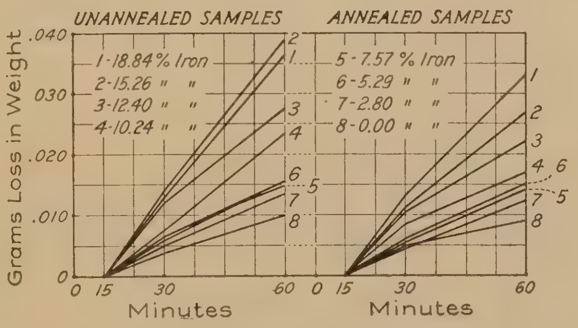

FIG. 7.—Shows effect (grams loss) of varying dissolved iron concentration in 11.45% muriatic acid at 85°F.

The increase in the rate of pickling with increase in ferrous iron concentration in hydrochloric (muriatic) acid, is the reverse of what we found in sulphuric acid, where increasing iron concentration lowered the rate of pickling. This is illustrated in Table VIII and Fig. 8, where total loss during the entire pickling period is plotted against concentration of ferrous iron, both in sulphuric and muriatic acid solution.

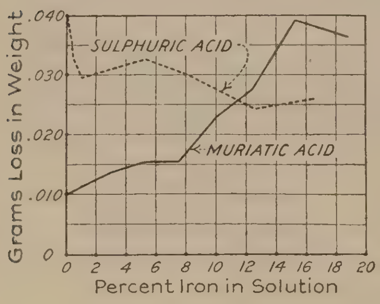

Fig. 8.—Shows effect (grams loss during 45 minutes pickling) of increasing dissolved iron concentration in pickling baths of sulphuric acid at 130°F and muriatic acid at 85°F.

No variations in acid strength or temperature were made with muriatic acid, as with sulphuric acid, but Conroy[1] found that the rate of pickling in less than 20% hydrochloric acid diminished but slightly with decrease in acidity, and that with each increase in temperature of 10°C (18°F) the rate of pickling doubled. This statement seems to be fairly well borne out in practice.

VI. Comparative Pickling Loss—Unannealed and Annealed Metal

In Table IX and Fig. 9, we have averaged all experimental determinations covered in the preceding data, to compare the total loss in weight of unannealed and annealed metal in the pickling process.

Table IX

Solution, 6.1% sulphuric acid at 130°F Dissolved iron content = 5.73% (calculated as av.)			Solution, 11.45% muriatic acid at 85°F Dissolved iron content = 9.05% (calculated as av.)		
Pickling time (minutes)	Loss unannealed sheets (gms.)	Loss annealed sheets (gms.)	Pickling time (minutes)	Loss unannealed sheets (gms.)	Loss annealed sheets (gms.)
7½	.0304	.1397			
15	.0364	.1446	15	.0497	.1733
30	.0479	.1504	30	.0582	.1813
60	.0672	.1594	60	.0723	.1921

These curves show the rapid loss in weight during the first few minutes of pickling, while the acid is attacking the scale and rust on the metal and the lessened attack during the succeeding minutes of pickling time.

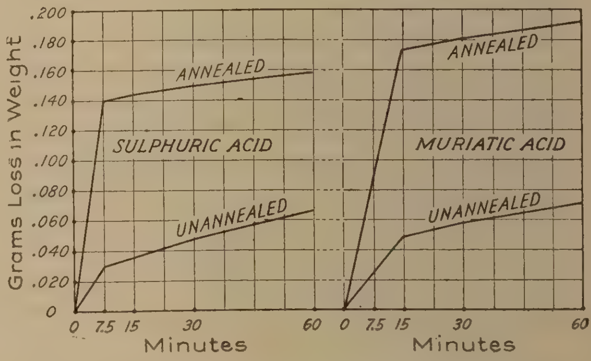

Fig. 9.—Shows comparative pickling loss of annealed and unannealed sheets in sulphuric acid at 130°F and in muriatic acid at 85°F.

VII. Influence of Monel Metal Basket

In the preceding experiments, all metal samples were simply immersed in the pickling solution in a glass beaker, so in order to approximate plant conditions more closely, where the ware to be pickled is usually placed in a basket of acid-resisting metal, other trials were made in which our samples were placed in a monel metal basket for pickling.

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[1] *Jour. Soc. Chem. Ind.*, **20**, 316–20 (1901).

It is interesting to note that our samples in this case all lost more weight, *i.e.*, pickled faster, when using the monel metal basket than when they were in contact only with the glass surface.

Table X and Fig. 10 show the comparative loss in weight of unannealed iron pickled in muriatic acid, using the monel metal basket and not using it.

A like increase in rate of pickling is found in sulphuric acid at 130°F, using a monel metal basket on either unannealed or annealed sheets, as may be seen from Table XI and Fig. 11.

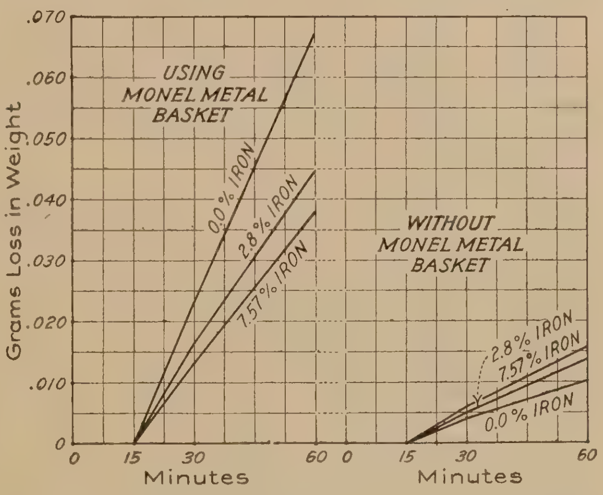

FIG. 10.—Shows rate of pickling in muriatic acid at 85°F when using monel metal basket, compared with rate of pickling without basket.

TABLE X

Ferrous iron content of 11.45% muriatic acid solution (%)	Using Monel Metal Basket		Without Monel Metal Basket	
	Loss 15–30 min. period (gms.)	Loss 15–60 min. period (gms.)	Loss 15–30 min. period (gms.)	Loss 15–60 min. period (gms.)
0.0	.0230	.0670	.0040	.0100
2.8	.0165	.0445	.0050	.0135
7.57	.0130	.0380	.0060	.0155

TABLE XI

Solution 6.1% sulphuric acid		Unannealed			Annealed		
		Loss 7½–15 min. period (gms.)	Loss 7½–30 min. period (gms.)	Loss 7½–60 min. period (gms.)	Loss 7½–15 min. period (gms.)	Loss 7½–30 min. period (gms.)	Loss 7½–60 min. period (gms.)
0.0 % dissolved iron	without monel	.0080	.0232	.0485	.0070	.0130	.0240
	with monel	.0165	.0440	.0870	.0105	.0250	.0485
5.16 % dissolved iron	without monel	.0065	.0185	.039	.0050	.0105	.0215
	with monel	.0115	.0300	.0740	—	—	—

An increase in the rate of pickling, due to the electrolytic potential difference between monel metal and iron, will in all probabilities, also be found at other acid temperatures and concentrations.

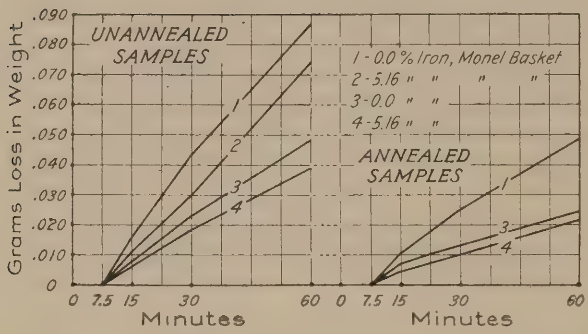

FIG. 11.—Shows comparative rate of pickling of annealed and unannealed sheets in 6.1% sulphuric acid at 130°F, using monel metal basket for samples.

VIII. Effect of Addition of Muriatic Acid and of Sodium Chloride To a Sulphuric Acid Pickling Bath

Some few plants in which sheet iron or steel is pickled use mixtures of sulphuric and muriatic acid for their pickling bath, or mixtures of sulphuric acid and sodium chloride (common salt), which reacts with the sulphuric acid to form a mixture of sulphuric acid, muriatic acid, and sodium bisulphate, according to the equation:

$$\text{Excess } H_2SO_4 + NaCl = H_2SO_4 + HCl + NaHSO_4.$$

Both sodium chloride and muriatic acid function as retarders of the action of sulphuric acid on iron, according to O. P. Watts[1] and this is evident from the data presented in Table XII and Fig. 12, where mixtures of muriatic and sulphuric acid (1% muriatic -5% sulphuric and 2% muriatic -4% sulphuric) were used at 130°F.

The retarding effect of the muriatic acid is evident from the curves in Fig. 12, and is all the more evident when we consider that although the total acid percentage composition of our baths are the same, the normality of our solutions increase when we substitute muriatic acid for sulphuric acid and hence our pickling bath is really "stronger."

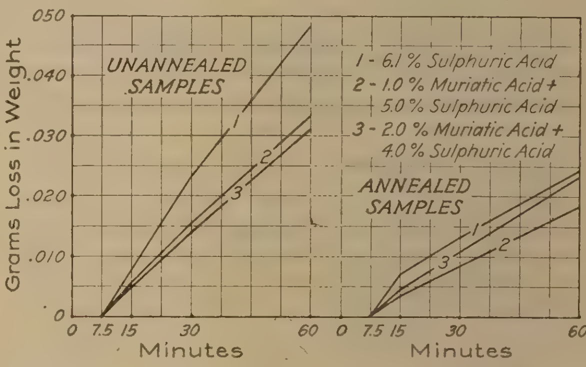

FIG. 12.—Shows retarding effect of muriatic acid in a sulphuric acid pickling bath, as compared to a straight sulphuric acid bath.

In Table XIII and Fig. 13, the effect of adding sodium chloride (common salt) to a sulphuric acid pickling bath is shown.

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[1] *Trans. Am. Elec. Soc.*, **21**, p. 337 ff. (1912).

TABLE XII

Solution	Unannealed Loss during 7½–15 min. period (gms.)	Loss during 7½–30 min. period (gms.)	Loss during 7½–60 min. period (gms.)	Annealed Loss during 7½–15 min. period (gms.)	Loss during 7½–30 min. period (gms.)	Loss during 7½–60 min period (gms.)
1% muriatic acid 5% sulphuric acid	.0055	.0155	.0335	.0035	.0085	.0180
2% muriatic acid 4% sulphuric acid	.0050	.0140	.0315	.0045	.0105	.0230
6% sulphuric acid	.0080	.0232	.0485	.0070	.0130	.0240

TABLE XIII

Solution	Unannealed Loss during 7½–15 min. period (gms.)	Loss during 7½–30 min. period (gms.)	Loss during 7½–60 min. period (gms.)	Annealed Loss during 7½–15 min. period (gms.)	Loss during 7½–30 min. period (gms.)	Loss during 7½–60 min. period (gms.)
6.1% sulphuric acid	.0080	.0232	.0485	.0070	.0130	.0240
6.1% sulphuric acid +2.5% sodium chloride	.0055	.0160	.0350	.0050	.0085	.0170
6.1% sulphuric acid +5% sodium chloride	.0055	.0150	.0350	.0060	.0120	.0225

It is quite evident that the addition of sodium chloride to the sulphuric acid bath retards the rate of pickling, and a small amount (2.5%) seems to be more effective than twice that amount.

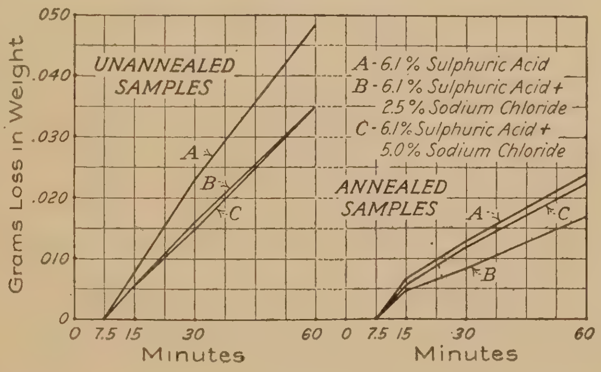

FIG. 13.—Shows retarding effect of addition of sodium chloride to sulphuric acid pickling bath.

IX. Conclusions

The results of this investigation show that a number of factors may influence the rate of pickling. Although these investigations necessarily had to be conducted along quantitative lines, the results and the following conclusions are stated along a qualitative or comparative basis, because other factors over which we have no control may also enter into the process.

(1) Increase of dissolved iron (ferrous sulphate) in a 6% sulphuric acid pickling bath at 130°F retards the rate of pickling.

(2) The data evidence no advantage in adding old pickle solution to a new sulphuric acid pickling bath.

(3) Increase of dissolved iron (ferrous chloride) in a 11.45% muriatic acid bath at 85°F increases the rate of pickling, although this is contrary to theory.

(4) Ferric sulphate in the sulphuric acid bath will accelerate the rate of pickling, but the difficulty of keeping this dissolved iron in the higher state of oxidation renders this fact of little commercial use.

(5) Decrease in acidity from 6.54 to 4.6% sulphuric acid lowers the rate of pickling, and vice versa, but

(6) Increase of pickling temperature accelerates the rate of pickling with sulphuric acid and will more than offset the weakening of acid in commercial use.

(7) Iron annealed at 1300°F for 1½ minutes loses from 250 to 400% more in weight during the early stages of pickling than unannealed iron, but there is less danger of "overpickling" the former.

(8) A monel metal basket in which the iron is placed in the pickling tank accelerates the rate of pickling.

(9) Addition of muriatic acid or sodium chloride to a sulphuric acid pickling bath, other conditions remaining constant, retards the rate of pickling.

THE ANNEALING OF GLASS—A NON-TECHNICAL PRESENTATION[1]

BY A. N. FINN

Introduction

The rapid reduction in the temperature of glass which is incident to practically all commercial molding almost invariably produces a condition in the glass commonly known as "strain."[2] This condition must, in general, be removed before the ware is satisfactory for commercial purposes and its removal is called annealing or tempering.[3]

Strain is due to an inelastic yielding under the stresses developed within the body of the glass while cooling, because at any moment during this time the different parts of the body are not contracting at the same rate. During molding the surface of the hot glass coming in contact with the relatively cold mold shrinks or contracts very rapidly and is quickly cooled to a temperature at which the glass is rigid. The interior loses its heat more slowly and, consequently, contracts less rapidly than the surface which must, therefore, if the stresses become large enough, either crack or yield inelastically.

After the surface becomes rigid or at least practically so, it does not yield readily to any force applied to it and tends to resist the contraction of the hotter and relatively soft interior as it continues to cool and contract. This produces stresses in the glass, the surface usually being compressed while the interior is dilated. If these stresses exceed the strength of the glass, it will break. This may occur either during the initial cooling or subsequently whenever the glass is subjected to sudden temperature changes, such as those resulting from the action of hot or cold water. In order to reduce the liability of breakage of ordinary ware to a minimum, glass must be annealed.

The annealing of glass consists of two fundamental steps. The first is to heat it to such a temperature that the entire body of the glass becomes sufficiently soft to permit it to yield. Then, if sufficient time be allowed, the stresses developed during molding will disappear. The second is to cool it so slowly that the temperature differences between the interior of the glass and its surfaces, with the consequent differences in contraction, are not great enough to produce objectionable strain.

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[1] Published by permission of the Director, Bureau of Standards. Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Atlanta, Ga., Feb., 1926. (Glass Division.) Received March 29, 1926.

[2] This is permanent strain and should not be confused with temporary strain resulting from the application of external force or temperature differences.

[3] Tempering sometimes means the intentional introduction of strain, as, *e.g.*, in the heat treatment of glass to produce special physical properties.

The Annealing Range

In order to anneal glass most successfully, it is necessary to know the temperature range in which it can be done. At too high a temperature the glass will soften so much that it will lose its shape. If the temperature is too low, either an excessive amount of time will be required or the glass will not be annealed.

Several methods have been recommended for determining the annealing temperature for a glass. Among them the "cut and try" method, the bending rod method,[1] the method of observing the glass in polarized light during heating,[2] the location of the region of abnormal heat absorption,[3] and the measurement of the variation of the expansivity with temperature[4] may be mentioned.

Of these the last two seem, in general, to be most satisfactory. The heat absorption method not only locates the annealing range but also gives an idea as to how the particular sample was annealed. The thermal expansion method gives, in addition to the annealing range, definite information regarding the thermal expansion of the glass.

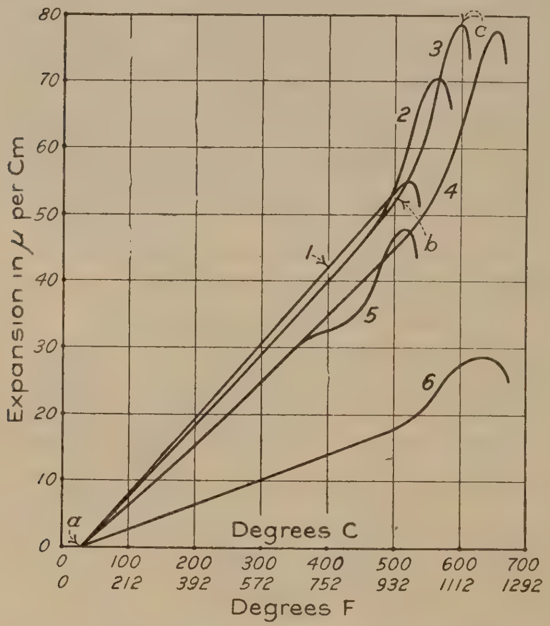

FIG. 1.—Thermal expansion curves of six glasses. See Table I for compositions.

Figure 1 is taken from data obtained at the Bureau of Standards[4] and shows the thermal expansion curves of several commercial glasses whose approximate compositions are given in Table I.

It will be noted that all the curves are similar except No. 1. This similarity consists of a fairly straight line from *a* to *b* (indicating a uniform expansion in that temperature range), an abrupt change at *b* (indicating an increased rate of expansion) and a reversal of direction at *c* (indicating a material softening of the glass).

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[1] English and Turner, *Jour. Soc. Glass Tech.*, **2,** 90 (1918).

[2] Tool and Valasek, Bur. Stand., *Sci. Papzr,* No. 358 (1920); Adams and Williamson, *Jour. Frank. Inst.,* **190,** 597–631; 835–70 (1920).

[3] Tool and Eichlin, *Jour. Amer. Ceram. Soc.,* **8,** 1–17 (1925); *Jour. Op. Soc. of Am. and Rev. Sci. Inst.,* **8,** 419–49 (1924).

[4] Peters and Cragoe, Bur. Stand., *Sci. Paper,* No. 393 (1920).

TABLE I

APPROXIMATE PERCENTAGE COMPOSITION OF GLASSES NOS. 1–6

	SiO_2	CaO	MgO	Na_2O	Al_2O_3	B_2O_3
1	74	5	3	17	1	–
2*	74	6	3	17	–	–
3	72	11	–	17	–	–
4	72	15	1	12	–	–
5		Lead Tubing				
6	81	–	–	5	2	12

* Computed from batch composition.

The ordinary commercial annealing range of any of these glasses (except No. 1) is between the points *b* and *c*. However, since the "yield" or "flow" of the glass at *b* is very slow, it would take at least several hours to anneal it at this temperature. At *c* the "yield" is usually very rapid and the stresses or "strain" in the glass will be dissipated almost as soon as the glass reaches this point.

Curve 1 does not show an increase in the rate of expansion comparable with the section *bc* of the curves for the other glasses, since the available data show that the rate of expansion of this glass is practically uniform from room temperature to its softening point. From such a curve it is impossible to determine the whole range in which the glass could be annealed, but it does locate a very narrow range (about 512°C, 954°F) near an apparent softening point. The use of this narrow range would require very accurate temperature control in order to anneal the glass without danger of overheating it. Preliminary thermal absorption measurements on the same glass indicate that the annealing range is between 500°C and 530°C (932°F and 986°F), which gives greater latitude in controlling leer temperatures. Although it was reported that this glass could not be annealed satisfactorily, this was successfully accomplished in the first trial at the Bureau of Standards by holding it at 512°C (954°F) (as indicated by the curve) for 20 minutes before cooling slowly.

Figure 2 shows the heat absorption curves obtained from three portions of a piece of window glass.[1] These curves have two points in common, one at about 500°C (932°F) where heat absorption begins and one at about 610°C (1130°F) where this absorption ceases. The temperature range in which heat is absorbed is regarded as the annealing range and is comparable with the range *bc* of curve 3 in Fig. 1. The vertical displacement of the curves in Fig. 2 is associated with the degree of annealing of the respective samples, the upper curve being obtained with a highly strained sample and the lower one from a well annealed sample.

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[1] Tool and Eichlin, *loc. cit.*

The Annealing Temperature and Time

Although stresses in glass are released very quickly at the maximum temperature of the annealing range, it does not follow that this temperature will be best suited for expeditious work.

Very thin ware can with safety be cooled rapidly from the maximum temperature, but the safe cooling rate decreases very rapidly as the thickness increases. Although the time required for annealing at lower temperatures is somewhat greater, it has been shown[1] that the use of lower annealing temperatures permits a more rapid cooling rate which more than compensates for the increased time for annealing.

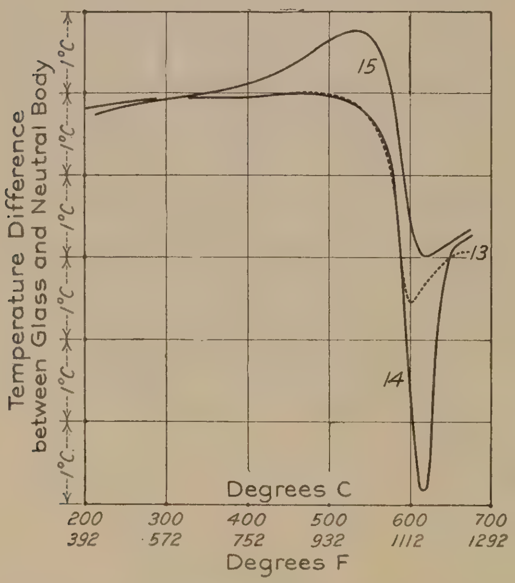

FIG. 2.—Heat absorption curves of a specimen of window glass. Curve No. 13, the original glass; No. 14 after annealing at 515°C; No. 15 after rapid cooling from 670°C.

The selection of the annealing temperature should then be governed by the thickness of the ware. An ordinary soda-lime glass which begins to soften at approximately 600°C (1110°F) can be annealed in about 30 minutes at 535°C (995°F), in two hours at 515°C (960°F), and in 10 hours at 490°C (914°F). These approximate the most satisfactory temperatures to use for ware whose thickness is 1, 2, or 5 cm.

The Cooling Rate

The cooling rate depends not only on the temperature from which the glass is cooled (the annealing temperature) but also on its thickness. Using the annealing temperatures mentioned above, the initial cooling rate for glass 1 cm. thick is about 100°C (180°F) per hour, for glass 2 cm. thick 25°C (45°F) per hour and for glass 5 cm. thick 4°C (7°F) per hour. But as the temperature falls, this rate can be increased, so that after the temperature has dropped about 35°C (63°F), it may become twice as great, *i.e.*, 200°C (360°F), 50°C (90°F), and 8°C (14°F) per hour and finally after a drop of 100°C (180°F), the rate per hour may be as high as 1500°C (2700°F), 400°C (720°F), and 60°C (108°F), respectively.

After this glass has been cooled below about 400°C (752°F), the rate may be increased still more without danger of introducing permanent strain unless the temporary strain developed exceeds the strength of the glass and breaks it.

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[1] Adams and Williamson, *loc. cit.*

Temperature Control

The foregoing statements are based on the assumption that temperatures can be accurately controlled, a condition which is hard to obtain in many of the commercial leers in use. However, it is suggested that properly installed base-metal (chromel-alumel) thermocouples, connected with a suitable temperature indicator will help to improve and control the quality of annealing obtained in any plant.

Needless to say, the greater the uniformity in the temperature of any zone in the leer, both from side to side and from top to bottom, the better the grade of the annealing will be.

Apparatus for Detecting and Estimating Strain

Strain in glass is easily detected by means of polarized light, but since this is not a technical paper, any attempt to discuss polarized light would be out of place. However, a discussion of the fundamental principles of a strain detector, scleroscope, or polariscope is not out of place. Regardless of the names these instruments may have, they all involve the same principle.

A beam of light (white light) is either reflected from or passed through a "polarizer" which in the first case is usually a plate of black glass or, in the second, a number (pile) of thin transparent plates and in both cases the surfaces of these plates must make a definite angle with the beam. The reflected or transmitted beam then passes through the sample being tested and is again reflected at the same angle as before from another plate of black glass or is passed through a second pile of plates set at the proper angle. In either case these are called the "analyzer" and they are sometimes replaced by a nicol prism. From the character of the light finally passing the analyzer the degree of annealing is determined. If the sample is free from strain, no change in the intensity of the field (as compared with the field when no sample is used) or in the appearance of the sample will be observed; if it is moderately strained, the light will be brighter in certain areas; and if it is highly strained, it will appear colored, and the color will vary over the field of view.

If the analyzer is a nicol prism, a sensitive tint plate may be advantageously used because this, in a way, intensifies the effects obtained with moderately strained glass by producing a series of colors which can be more easily interpreted and compared with those obtained in testing other (standard) samples.

The apparatus used at the Bureau of Standards for determining the "amount of strain" or the degree of annealing is so simple in construction and yet so eminently satisfactory that a detailed description of it will be given. (See Fig. 3.)

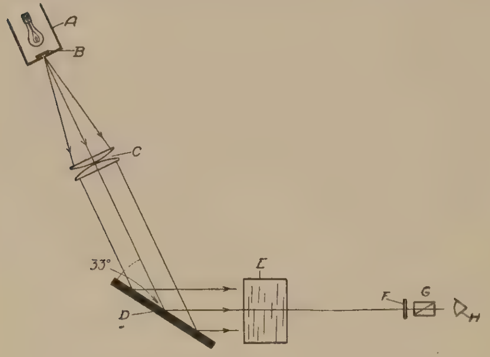

FIG. 3.—Sectional view of polariscope for testing glass for strain. *A*, source of illumination; *B*, ground glass; *C*, condensing lens; *D*, black glass plate (polarizer); *E*, sample to be tested; *F*, sensitive plate; *G*, nicol prism (analyzer); *H*, observer's eye.

Source of Light A 200-watt electric light bulb is enclosed in a box made of bright sheet metal. A ½-inch hole is cut in one side of the box and covered with a piece of glass whose surface is "fine" ground. This small piece of glass, illuminated by the lamp, is the actual source of light.

A condensing lens, 7 inches in diameter and having a 15-inch focal length, is so placed that its focus is at the "source of light." The light after passing through the lens is practically a parallel beam, but not entirely so since the source is not a "point."

Polarizer The beam of light then strikes a piece of polished black glass at an angle of approximately 33° (between the beam of light and the glass) or the angle which is necessary with the particular glass for obtaining the best polarization possible.[1] Although the beam of light reflected from the black glass is apparently not affected, it is, nevertheless, polarized.

Analyzer At some distance in front of the black glass polarizer a nicol prism is placed in the polarized beam, so that the enlarged image of the "source" is visible through it. By turning the nicol, the intensity of the light will change progressively from bright to dark. The nicol is properly set when the field is as dark as possible.

Tint Plate The tint plate, which should be a "First Order Purple" (retardation, about 575$\mu\mu$), is mounted directly in front of the nicol prism and is set by turning it until the color of the light passing through the prism is as marked as possible. Nicol prisms and

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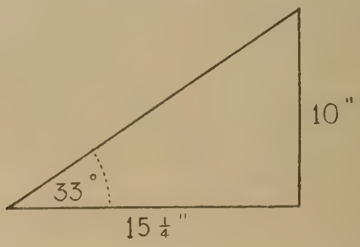
[1] An angle of 33° can easily be obtained as follows: Draw a right triangle with one side 15¼ inches and the other side 10.0 inches long. The angle between the long side and the hypotenuse will be about 33°. Thus:



tint plates can be obtained from practically any dealer in optical instruments.

If, now, a piece of strained glass is placed in the beam of light between the polarizing plate and the nicol, parts of the glass will apparently be colored differently than the original field. If well-annealed glass is examined, practically no change in color will be seen and if a highly strained piece of glass is used, the colors will be vivid. If the tint plate is removed and the same pieces of glass are examined, the first (moderate strain) will appear brighter in certain areas, the second (no strain) will produce no change, and the third (high strain) will be very bright or even colored in some places.

Irregular Shapes Some ware, on account of its irregular shape, can not be examined satisfactorily without putting it in a "tank." An immersion tank with two plate glass windows[1] (which should be free from strain) is satisfactory for this purpose and for best results it should contain a liquid whose index of refraction is as near as possible to that of the glass being tested.[2] Water or solutions of salts in water are better than nothing, but some organic liquids are much superior. Monochlor-benzene is very satisfactory for most soda-lime glasses; its odor is not disagreeable, but it is somewhat flammable and should not be used in too close proximity to fires. Carbon tetrachloride, although it does not have quite the right index of refraction, is much better than water and the fire risk is almost negligible.

Temperature Changes Glass being tested should be absolutely uniform in temperature. Ware taken from a room warmer or colder than the room in which the testing is done will show different amounts of strain than if allowed to come to thermal equilibrium. Even the effect of the heat from an inspector's hand will be pronounced, especially if the ware is thick. Ware directly from the leer may look very bad or very good, but after becoming cool it may look quite different.

Position of the Ware The exact position in which a piece of ware should be placed in the field of the polariscope is difficult to define, because it depends on the shape of the ware. However, this can be determined by examining the piece while gradually changing its position, the one desired being that in which the greatest change in intensity or coloration is observed.

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[1] Glass can be cemented to metal with a mixture of glue and plaster of Paris if the tank is to contain non-aqueous liquids, or with shellac and powdered flint if aqueous liquids are to be used.

[2] When the immersion liquid matches the glass, the immersed sample becomes practically invisible.

General Considerations

The question, "How well should glass be annealed" is frequently asked. There is no definite reply to this except to say that it should be sufficiently free from strain to serve the purpose for which it is intended. This can only be determined by experience, but with similar shapes in different sizes, the larger pieces should be more carefully annealed than the smaller ones.

The majority of ware should probably be very well annealed because practically all of it is subjected at times to sudden temperature changes. This is especially true of hollow ware, which is repeatedly washed with hot water or steam and then cooled rapidly. Plate and window glass might be stronger if it were not completely free from permanent strain because it would then be better able to withstand pressure, such as that produced by wind.

Standards The use of standard samples for controlling the effectiveness of the annealing operation is probably the most satisfactory method. Comparison of the daily work with such standards gives a definite idea of what is going on in the leer, and frequent comparison with properly selected standards will unquestionably assist glass manufacturers in determining and maintaining the conditions necessary to anneal their glass properly and consistently.

METHODS OF TESTING AND THE PHYSICAL PROPERTIES OF WET-PROCESS ELECTRICAL PORCELAIN[1]

By Louis Navias[2]

ABSTRACT

Data are given for the compressive, transverse, and tensile strengths of wet-process electrical porcelain.

Compressive Strength The height of the sample is an important variable. Initial failure and ultimate failure are discussed and it is suggested that as the latter is the more definite and constant of the two, the ultimate failure be always determined and recorded as the "compressive crushing strength." The cylindrical specimen 1 sq. in. in area ($1\frac{1}{8}$ in. diameter) and $1\frac{1}{8}$ in. high is recommended.

Transverse Strength The load applied to cause rupture is directly proportional to the cube of the diameter of the cylinder over a wide range of diameters. A cylinder with an area of 1 sq. in. is suggested. Cylindrical specimens give constant and high values.

Tensile Strength As the area of minimum cross-section increases the tensile strength decreases rapidly. The diameter should be given with determined values. An apparatus for making tensile strength determinations on a specimen with conically shaped ends and minimum area of 1 sq. in. is described.

Relationship of specimen size and effective dimensions to the average general dimensions of the ware and their methods of manufacture is discussed.

Introduction

In the last few years interest has been aroused in the subjects pertaining to the physical testing of porcelain to the extent that the American Society for Testing Materials included in its specifications some methods of testing issued under its designation D116–21T and reprinted in 1924 as D116–24T. These methods are tentative and subject to revision. Since then tests have been made and new methods of testing have been devised by interested groups. The purpose of this paper is to present the results of the work in order to create further interest and to give some definite information upon which discussion and future work may be based. Parenthetically it may also be stated that the literature of the American Ceramic Society is lacking not only in such data but also in the critical survey of the tests themselves which makes for better comprehension of the numerical results obtained from the tests.

The statement cannot be over-emphasized that the physical properties of a material like porcelain made by the wet-process method are dependent upon the batch composition, the methods of working in the green state, and upon the firing, and that changes in these processes are reflected in the physical properties. Of the possible defects the working in the green state is especially interesting in the study of testing, for the final shape and constitution of the porcelain test specimen are dependent on the methods involved and on the precautions taken.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (White Wares Division.)

[2] Research Laboratory, General Electrical Co., Schenectady, N. Y.

Tamping by hand in a rectangular mold has long been a common practice. There is no need here to dwell on the subject of flaws, as air pockets, surfaces of contact between two separately tamped layers, rough edges, and the like, that are prevalent. Test specimens have also been obtained from a column extruded through a die with such machines as pug mills, screw, and hydraulic presses. Each type of ware is usually manufactured from a blank of plastic material obtained by one of these processes, and it appears reasonable to suggest that the test specimens should be made under similar conditions where possible. Laminations and segregations will always have to be guarded against, not only in the commercial practice but also in the experimental and testing practice.

For a number of reasons the writer has felt that a cylindrical specimen is better adapted for most physical tests than a specimen with a square, rectangular, or "rounded corner" square cross-section. Circular dies are most used in the manufacture of electrical porcelain. Sections of the cylindrical column after drying can be further worked or formed into test specimens and trued to shape and dimensions by turning in a lathe, the specimen being held either by one or both ends and worked down by metal tools or abrasive wheels. The perfection of manipulation in the production of test specimens is always desirable.

The dimensions of the test specimen are important from two considerations. In the first place, where possible, the test specimen should compare with the general type of merchandise under consideration in at least one dimension, which will usually be the thickness. Dishware, spark plugs, and bushings may be made from the same porcelain, and the test specimens representative of these widely different articles should show corresponding effective dimensions. From a second consideration there should be some proximity and correlation between effective dimensions of specimens used in different tests. Calculations are usually made and expressed in units as lbs. per sq. in. or kg. per sq. cm., quite often necessitating the use of large factors to obtain the common units. For any one particular property quite often no relationship has been found between changes in dimensions and the corresponding changes in the property under investigation. By association, such data of different properties as for instance tensile and compressive strengths may be correlated and false conclusions drawn. Until more information is obtained for the correlating of these values, the practice of stating the exact dimensions of the test specimens together with the calculated unit values is very commendable.

In the present case a cylinder whose area is 1 sq. in. (diameter $1\frac{1}{8}$ in.) has been taken to fulfill the conditions enumerated above. Where the height of the cylinder is involved as a variable in the calculation or where the height plays an important part although not specifically included in the formula (as for instance in compressive strength) it has been felt desirable to maintain it near the value of 1 to $1\frac{1}{8}$ in. It is anticipated that other properties and the methods of obtaining them will be forthcoming as time permits.

Compressive Strength

The A.S.T.M. specifications D116–21T call for a specimen cylinder $1\frac{1}{2}$ in. in diameter and 1 in. high with ground plane parallel surfaces. In test, the specimen is to be placed between contact pads of blotting paper $\frac{1}{32}$ in. thick. For this test the writer has advocated a specimen $1\frac{1}{8}$ in. diameter and $1\frac{1}{8}$ in. high, the height being equivalent to the diameter. Others have advocated that the height should be at least twice the diameter, Riddle and Laird[1] using a specimen 1 in. diameter and $2\frac{1}{2}$ in. high.

Effect of Height of Specimen on Compressive Strength

The height of the specimen does not enter into the calculation for determining the compressive strength per unit area but nevertheless it plays an important part in the magnitude of the result. Table I gives a number of examples. The specimens were cut from cylinders of plastic material squirted through a die in a hydraulic press. When dry the opposite faces were rubbed down nearly parallel, and after forming they were ground parallel. In experiment No. 130 doubling the height decreases the average crushing strength from 58,100 to 42,800 lbs. per sq. in., a lowering of 26%. In experiment No. 318 increasing the height by one-half lowers the average crushing strength from 75,700 to 58,100 lbs. per sq. in., a lowering of 23%, whereas doubling the height decreases the crushing strength from 75,700 to 49,400 lbs. per sq. in., a decrease of 35%. The height is an important function of the values obtained for compressive (crushing) strength.

Initial and Ultimate Failure

Porcelain is a brittle material and its behavior under compression is unlike materials which flow under stress. As the load is applied to the porcelain specimen two failures are generally noticeable. The initial failure manifests itself by some disturbance around the specimen, as for

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[1] F. H. Riddle and J. S. Laird, "The Tensile Strength of Porcelain," *Jour. Amer. Ceram. Soc.*, **5**, 385 (1922).

instance, caused by the spalling of chips of porcelain. At other times no disintegration is visible although there has been a very decided tremor which would indicate that there has been a readjustment in the parts of the machine. These readjustments may sometimes be due to unequal speed of application of the working load. In most cases, however, initial failure is accompanied by a fracture of the specimen parallel to its height and parallel to the direction of the application of the load, the specimen usually being severed into two halves. This observation has also been recorded by Riddle and Laird[1] who state, "Failure under test with the specimens was a little peculiar as in most cases there first occurred a splitting of the specimens into longitudinal segments." In all cases the specimens remained in position in the machine, and considerable load had to be applied before the ultimate compressive (crushing) strength was attained. In some instances there was no aural evidence of initial failure and the only values obtained were ultimate crushing strengths.

The recognition of the initial failure is greatly dependent upon the alertness of the operator of the testing machine, whereas the ultimate failure is unmistakable for the specimen is literally crushed into numerous small fragments with great force, and the event takes place in a very short period of time. It is a dangerous practice to view the specimen during the process of compression, for particles may be thrown off with high velocity at any time.

In Table I values are given for the loads at initial and ultimate ailure. From the ultimate load and the dimensions of the specimen the compressive (crushing) strength is calculated. The numbers in parentheses in the column "Initial Failure" refer to the number of specimens for which values of initial failure were obtained. The difference between this number and the total number of specimens in each group gives the number of specimens for which no initial failure was observed. No numerical relationship can be found to exist between the loads applied at initial and ultimate failures, although it would be expected that as the height of the specimen was increased the divergence between initial and ultimate loads would decrease. In experiment No. 130 doubling the height made great differences in the actual values of initial and ultimate load, but no difference in the ratio between them, the initial failure occurring at a value 47% of that of the ultimate failure. In experiment No. 318, the ratios are respectively 49, 54, and 71% as the height is increased. On account of the uncertainties connected with the determination of the initial failure the writer feels

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[1] *Jour. Amer. Ceram. Soc.*, **5**, 59–61 (1922) Part II.

TABLE I

COMPRESSIVE STRENGTH

EXPERIMENT NO. 130 FIRED TO CONE 10

Specimen no.	Av. height	Av. diameter	Initial failure load in lbs.	Ultimate failure load in lbs.	Compressive crushing strength lbs. per sq. in.
6	0.760″	1.467″	(4) 46,500	98,300	58,100
Maximum					72,000
Minimum					49,300
Average deviation from the mean	1.05%	0.61%			9.3%
6	1.508″	1.479″	(6) 34,700	73,400	42,800
Maximum					47,000
Minimum					36,500
Average deviation	1.00%	0.41%			8.2%
EXPERIMENT NO. 318 FIRED TO CONE 10½					
10	2.277″	1.091″	(9) 32,900	46,100	49,400
Maximum			44,000	62,000	66,900
Minimum			26,000	34,000	36,700
Average deviation	0.4%	0.5%	14.7%	12.8%	12.2%
10	1.714″	1.092″	(9) 29,200	54,400	58,100
Maximum			40,500	62,500	66,500
Minimum			24,000	42,000	44,700
Average deviation	0.5%	0.4%	13.0%	7.2%	7.1%
10	1.139″	1.096″	(7) 35,000	71,300	75,700
Maximum			45,000	80,500	84,300
Minimum			26,000	57,500	61,900
Average deviation	0.6%	0.5%	18.9%	9.4%	9.1%
EXPERIMENT NO. 178 FIRED TO CONE 9 (UNDERFIRED)					
6	1.44″	1.072″	(6) 32,500	52,100	57,900
Maximum					67,000
Minimum					51,000
Average deviation	0.7%	0.9%			10.6%
6	1.139″	1.081″	(6) 30,900	53,200	58,000
Maximum					72,000
Minimum					48,600
Average deviation	1.3%	0.6%			12.6%

that its determination should be merely an incidental observation in the determination of the ultimate compressive (crushing) strength. There would be greater clarity of purpose and no confusion with regard to the failure concerned in the test, if the test were named "compressive crushing strength," or by some phrase including the word "crushing."

Experiment No. 178 indicates the effect of underfiring on the compressive strength. The results should be compared with those of Experiment No. 318 for the same sized specimen.

Transverse Strength (Modulus of Rupture)

In the *1921–22 Yearbook*[1] *of the American Ceramic Society* a tentative method for transverse strength requires a "green" specimen in the shape of a bar 7 in. long and 1 in. square cross-section, to be broken on knife edges 5 in. apart. No reference is made to the testing of fired specimens. The A.S.T.M. makes no mention in its tentative or approved specifications of a transverse strength test for porcelain.

Cylindrical Specimen The following tests were made on cylinders of fired wet-process electrical porcelain. The cylinders are 6 in. long and were broken while supported on a span of 5 in. The block supports and the inverted wedge to which the load was applied, were made of triangular shaped steel blocks, the contact angle 45°, and the edges rounded to 0.125 in. radius. The modulus of rupture is calculated from the formula:

$$M = \frac{8\,PL}{\pi d^3}$$

where M = modulus of rupture
P = load in lbs. at rupture
L = distance between supports in inches
π = 3.1416
d = diameter of specimen in inches

In Table II are given data of the modulus of rupture on a number of specimens. One series, experiment No. 130, was made to determine the effect of changes in diameter. Throughout a wide range of diameters the modulus remains the same, indicating that the load at rupture is directly proportional to the cube of the diameter. The maximum variation in diameter of the cylinders was roughly threefold, with a corresponding variation in area of sevenfold and variation in d^3 of twentyfold.

Comment on the test has been made to the effect that a round specimen gives only point contacts for support and that such a condition may cause a decrease in the apparent strength. Sufficient data have been presented to show that the values are quite consistent. Felix Singer[2] gives for the highest value of the modulus of rupture of a number of porcelains, 855 kg. per sq. cm. equivalent to 12,200 lbs. per sq. in., the average value being much lower. Rosenthal[1] gives the maximum value of 590 kg. per sq. cm. for electrical porcelain, corresponding to 8,400 lbs. per sq. in. These facts are included to show that the data obtained with a cylindrical specimen give not only consistent but high values as well. A specimen with flat surfaces is subject to the requirement that the faces in contact with the wedges must be not only truly plane but also parallel in order to present line contacts and to prevent shear. Warping during firing is a much more serious condition with a flat-faced specimen than with a cylinder.

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[1] *Jour. Amer. Ceram. Soc.*, 5, 59–61 (1922). Pt. II.

[2] Felix Singer "Die Keramik in Dienste von Industrie und Volkswirtschaft," p. 472 (1923).

TABLE II

TRANSVERSE STRENGTH

EXPERIMENT NO. 130 FIRED TO CONE 10

Specimens	Diameter in in.	Av. deviation	d^3	Load in lbs.	Modulus of rupture Lbs. per sq. in.	Modulus of rupture Av. dev.
6	0.489	0.82%	.117	95	10,300	3.4%
6	0.749	0.27	.420	281	8,500	5.6
6	1.011	0.30	1.027	850	10,500	1.9
6	1.121	0.54	1.403	1120	10,200	4.4
6	1.113	0.27	1.371	1104	10,200	4.7
5	1.335	1.4	2.362	1855	10,000	4.2
6	1.345	0.45	2.422	1938	10,200	5.9
		EXPERIMENT NO. 198 FIRED TO CONE 8½				
6	1.103	0.46%			12,100	5.7%
		EXPERIMENT NO. 198 FIRED TO CONE 11¼				
6	1.106	0.54%			11,000	5.3%
		EXPERIMENT NO. 197 FIRED TO CONE 10				
6	1.102	0.27%			11,500	2.6%

Tensile Strength of Porcelain

Riddle and Laird[2] have described in detail a method for the determination of the tensile strength of porcelain, with specimens whose area at the minimum cross-section was 0.135 sq. in. (a diameter of 0.4 in.). This method has been included in the tentative specifications of the A.S.T.M., D116–21T. It is readily acknowledged that the test is applicable to the size of specimens advocated, but it is a question whether the tensile strength expressed as so many lbs. per sq. in., obtained from testing a specimen whose area is only 0.135 sq. in., can be considered as the tensile strength of the same material when the determination is made on a specimen whose minimum cross-section area is actually 1 sq. in. Riddle and Laird have given the answer to this question in the same paper, where they have plotted the tensile strengths of porcelain specimens against the area and diameter. The results for the larger specimens given below were determined from their graphs, as the actual values are not given.

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[1] In Searle's, The Chemistry and Physics of Clays and Other Ceramic Materials, p. 178 (1924).

[2] F. H. Riddle and J. S. Laird "The Tensile Strength of Porcelain." *Jour. Amer. Ceram. Soc.*, **5**, 385–93 (1922).

TENSILE STRENGTH IN LBS. PER SQ. IN.

Diameter (in.)	Special porcelain	Triaxial porcelain
0.4	9,500	5,800
1.125	7,300	*4,600
2.25	4,300	2,800

* Found by interpolation.

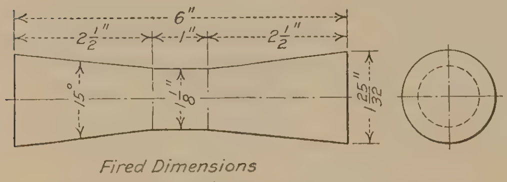

FIG. 1.—Test specimen for determining tensile strength of porcelain.

Although the area of minimum cross-section enters into the calculation of the tensile strength, the tensile strengths decrease rapidly as the area is increased. It seems therefore necessary to require that test specimens have such critical dimensions which will make them comparable with and representative of thicknesses of the material as used in practice. For spark plug porcelains a small specimen similar in dimensions is desirable and for much heavier articles as bushings of electrical porcelain a larger specimen is required. If such differences are recognized there should be no difficulty in interpreting the facts when the practice is followed of giving the diameter of the specimen as well as the calculated tensile strength.

New Apparatus for Tensile Strength In the present instance an apparatus has been developed for determining the tensile strength of a porcelain specimen whose minimum section has an area of 1 sq. in. Fig. 1 represents the specimen. Specimens 5

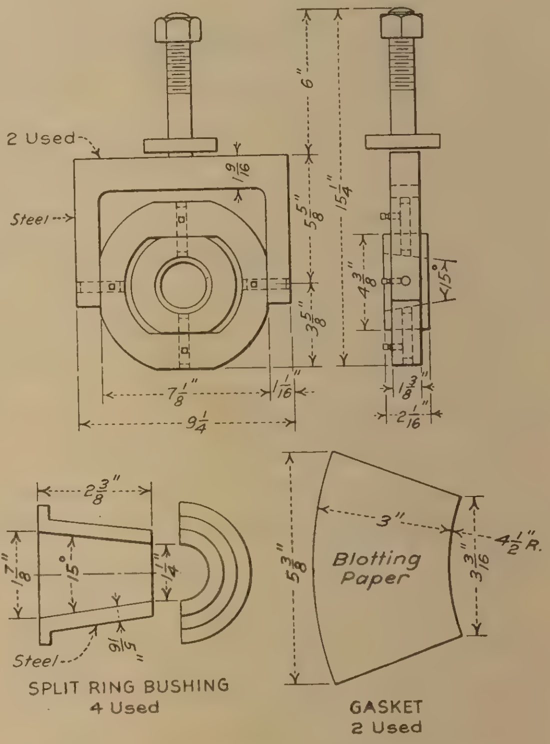

FIG. 2.—Grips used in determining tensile strength of porcelain.

inches long instead of 6 inches may be used as effectively. Of main importance is the correct angular and conical tapering to give a good fit in the grips of the apparatus. The specimens are usually turned from a cylinder on a lathe using a cutting metal tool or an abrasive wheel. Figure 2 gives the details of construction of the parts of the apparatus, while Figs. 3 and 4 show views of the apparatus in the test machine.

A suitable grip for holding the specimen in the tensile machine is shown, in which two grips are used. The split ring bushing fits into a conical retaining ring, which swings on two pins within an outer retaining ring, the latter being pivoted on pins in a yoke. The two retaining rings are thus pivoted at right angles to each other. The two yokes may also be placed at right angles to each other.

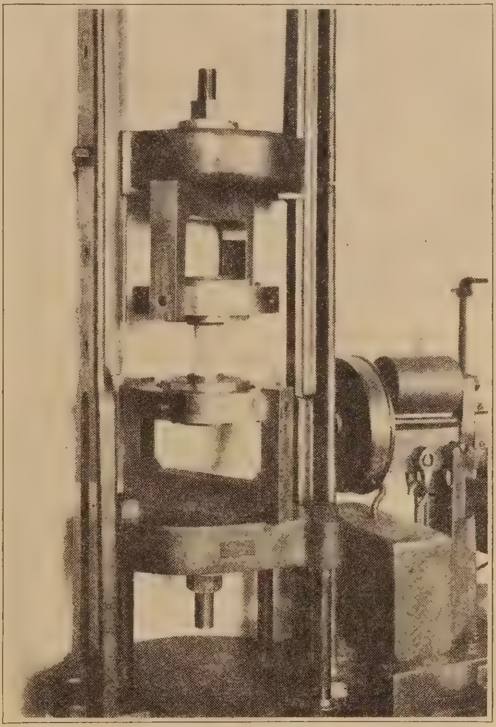

FIG. 3.—Grips and test specimen assembled in testing machine for determining tensile strength of porcelain.

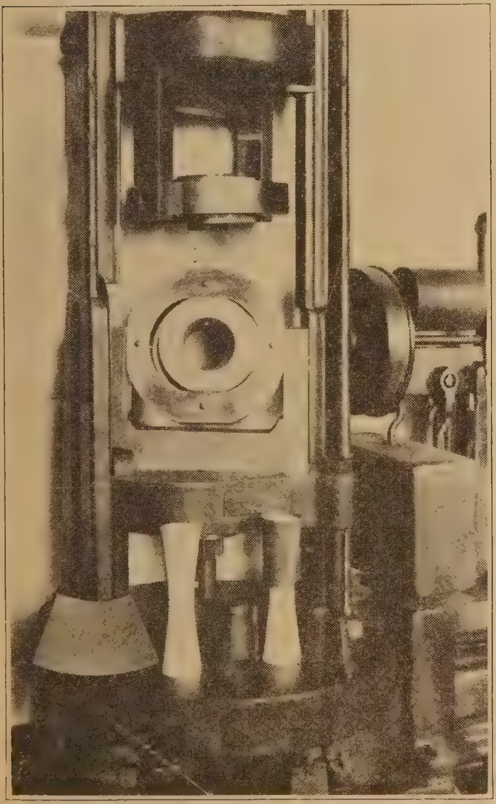

FIG. 4.—Disassembled view of grips and test specimen for determining tensile strength of porcelain.

Blotting paper gaskets $\frac{1}{64}$ in. thick, or sheet lead gaskets $\frac{1}{32}$ in. thick have been used. The blotting paper gaskets are cut to fit and are temporarily held in place during the assembling by a simple wire clamp. During the tension the blotting paper of a number of trials was found to have been compressed from 18 mils to 14.2 mils, namely by $\frac{1}{5}$ of the thickness.

Results on a set of samples are given in Table III. The results are particularly uniform and give not only a high value for the tensile strength but also a small percentage average deviation from the mean.

TABLE III

TENSILE STRENGTH

EXPERIMENT NO. 130 FIRED TO CONE 10

Specimen no.	Diameter at break (in.)	Cross-section (area)	Tensile strength lbs. per sq. in.
1	1.120	0.985	7130
2	1.047	0.860	6540
3	1.048	0.862	7030
4	1.061	0.882	7090
5	1.090	0.932	7280
6	1.075	0.909	7060
		Average	7020

Average deviation from the mean 2.3%

EXPERIMENT NO. 329 FIRED TO CONE 9½ IN MUFFLE KILN

Specimen no.	Diameter at break (in.)	Cross-section (area)	Tensile strength lbs. per sq. in.
1	1.084	0.923	6030
2	1.068	0.895	6940
3	1.090	0.934	7100
4	1.075	0.907	5660
5	1.084	0.924	5940
6	1.083	0.921	6040
		Average	6290

Average deviation from the mean 7.8%

Sets of specimens not fired as well as these give lower values with greater deviations, as illustrated in Experiment No. 329. In this case lead gaskets $\frac{1}{32}$ in. thick were used.

Conclusions

Compressive Strength (1) The height of the porcelain specimen is an important function and should be noted, although it does not appear in the calculation.

(2) The initial failure cannot be considered a critical property of the porcelain as its determination is greatly dependent upon the working of the testing machine and the alertness of theoperator.

(3) The ultimate failure is a definite unmistakable event. To eliminate confusion with the determination of initial failure, the ultimate failure should be designated as the "compressive crushing strength."

(4) There is no advantage in increasing (or decreasing) the height of the specimen above (or below) the 1 to 1 ratio of height to diameter.

Transverse Strength (1) Over a wide range of diameters the load applied to cylindrical specimens of porcelain to cause rupture is directly proportional to the cube of the diameter of the cylinder, yielding a definite value for the modulus of rupture.

(2) With a cylinder supported on straight-edged wedges, consistent and high values for the modulus of rupture are obtained.

Tensile Strength (1) The tensile strength increases as the cross-section of the specimen decreases, but no mathematical relationship has been found to exist between them. For this reason values of tensile strength given in conventional units should be accompanied by the dimensions of the specimen.

(2) An apparatus for making tensile strength determinations on a specimen, with conically shaped ends, of minimum area 1 sq. in. is described.

In general it has been found that for electrical porcelain effective dimensions of 1 inch (and areas of 1 sq. in.) for test specimens in compressive, transverse, and tensile strength tests are suitable. The actual dimensions and the methods of testing are given.

The writer wishes to acknowledge the aid given in the testing of the specimens by Frank L. Michael of this Laboratory and by the members of the staff of the General Engineering Laboratory.

SOME PROPERTIES OF FUSED QUARTZ AND OTHER FORMS OF SILICON-DIOXIDE[1]

By H. L. Watson[2]

ABSTRACT

A compilation of data on the physical properties of silicon-dioxide.

Introduction

The purpose of this paper is to set forth under one heading, the data on quartz in its various forms scattered throughout the technical press where it can be obtained only at the expense of considerable time and often of considerable effort.

The data was selected with a view toward covering the various characteristics, and no pretense is made as to a complete bibliography of data available. Neither is it the purpose to discuss the very excellent development of processes and manufacture of fused quartz products resulting from the work of E. Thomson, E. R. Berry, P. K. Devers, L. B. Miller, S. Boyer, B. F. Nieder, I. F. Hooper, E. Herzog, D. P. Gallant, and H. L. Watson, of the Thomson Research Laboratory, of the General Electric Co. at Lynn, Massachusetts, which work constitutes the subject matter of several papers before prominent technical societies.

The oxide of silicon (SiO_2) is found in many allotropic forms. Silica is one of the constituents of granite, gneiss, and other crystalline rocks. It forms quartzite and sandstone, and composes the mass of sand at the seashore. As quartz, it occurs crystallized and massive, and in both states is widely distributed. When crystallized it commonly exists in hexagonal prisms, terminated by hexagonal pyramids. It belongs to the rhombohedral division of the hexagonal system and its forms are sometimes very complex. Silica occurs in cryptocrystalline and amorphous forms which are anhydrous or physically hydrated. The crystalline forms are generally anhydrous, as quartz, tridymite, and cristobalite, although lussatite (a fibrous variety of tridymite) contains 7% of water.

"The average composition of the lithosphere is very nearly that of the igneous rocks alone."[3] Since average igneous rock contains approximately 60% silicon-dioxide it follows that the earth's crust contains nearly the same percentage of this material. Clarke gives 59.77 as the most probable value for the percentage of silicon-dioxide in the lithosphere. The percentage of SiO_2 in the mass of the earth, of course, is not known and cannot be estimated.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb. 1926. (Glass Division.)

[2] It is desired to acknowledge the service of J. W. Johnson of this Laboratory in compiling these data.

Thomson Research Laboratory, General Electric Co., Lynn, Mass.

[3] F. W. Clarke, The Data of Geochemistry.

An amorphous anhydrous product is obtained by the fusion of any of the natural forms of silica. Natural fused quartz is found in several igneous rocks.

Silica fused by lightning has been found in many countries, particularly in the form of long tubes, $\frac{1}{4}$ to $\frac{1}{2}$ in. in diameter, produced by the passage of the electric discharge through a bed of silica sand. These are known as fulgurites or Le Chatelierite, and were first observed in 1711 by Herman in Silesia, and attributed to lightning by Dr. Hentzen, in Westphalia, in 1805. Darwin in the "Voyage of H. M. S. Beagle" refers to the Uruguayan fulgurites.[1]

The various forms of silica can be catalogued with reference to their physical structure. The allotropic varieties of crystalline silica are as follows: crystallized silica in the form of quartz, tridymite, and cristobalite.

Each of these crystalline varieties of silica has at least two forms. The different forms have different physical and even chemical properties. Under certain conditions and at definite temperatures, transformations of state may take place. The transformations are reversible.

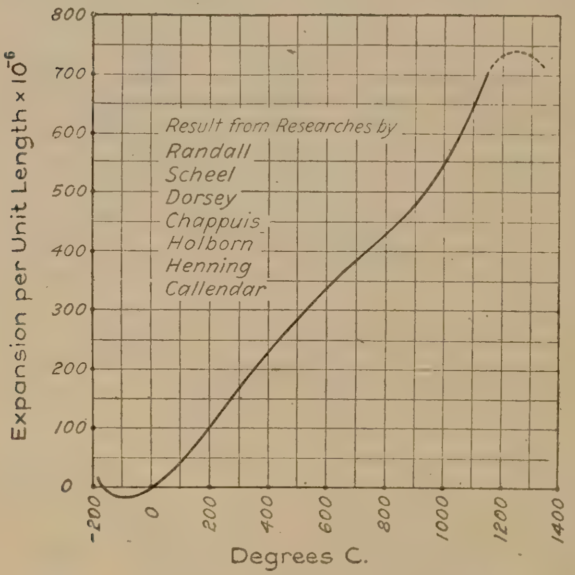

FIG. 1.—Thermal expansion of fused silica.

Quartz

At atmospheric temperatures crystal quartz can exist only in the α state. As already stated, it occurs in abundance. The luster is vitreous, or in some cases, greasy to dull. Colors of quartz specimens are various, as white or milk white, (milk quartz); purple or bluish violet (amethyst); smoky yellow or brown (smoky quartz) or Cairngorm stone, called morion when black or nearly so; yellow false topaz or citrine; aventurine, spangled with scales of mica or hematite; sagenite, containing acicular crystals of rutile; the cat's-eye, opalescent through the presence of asbestos fibers; and others.[2]

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[1] Richard Paget, Fused Silica.

[2] Century Dictionary.

The cause of the color in rose quartz has been investigated by E. F. Holden.[1] The evidence obtained favors the conclusion that this variety of quartz is colored by the presence of trivalent manganese. The color of rose quartz can be closely imitated by dissolving less than 0.01% of manganese in a silica gel. In this case as in actual rose quartz, the color disappears on heating to the transition temperature of 575°C. The same author has shown that the color of citrine, like that of colloidal solutions of ferric hydrate, is due to submicroscopic particles of hydrous ferric oxide.

"The effect of radium radiations on white or rose quartz is invariably to produce a dark smoky color, and it is interesting to notice that smoky quartz is a constant associate of radioactive minerals in Madagascar and Ontario, whereas rose quartz is not."[2]

Colorless crystal quartz is generally known as rock crystal. As stated, it commonly occurs in hexagonal prisms terminated by hexagonal pyramids. Some of the corners are, however, modified by small faces of other type. In crystallography, α quartz is placed in the trapezohedral class of the trigonal system, possessing three-fold symmetry about a vertical axis. Optically it is remarkable as exhibiting the phenomenon of circular polarization, the right and left hand character of the crystals optically corresponding to the arrangement of trapezohedral planes present.[3]

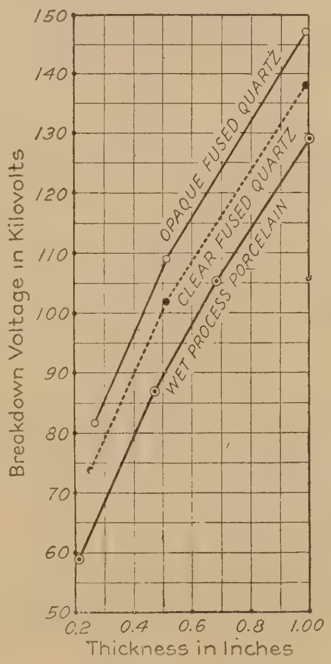

FIG. 2.—Dielectric strength of quartz and porcelain. Tests made under oil at 25°–60 cycles–1 in. spherical electrodes. Voltage raised 1 kv. per second from 0.

The symmetry of quartz crystals is, in fact, only ternary, and not hexagonal. One rhombohedron, generally better developed than the other, is said to belong to the direct form (with corrosion striae perpendicular to the axis) and the other to the inverse form. The two forms of rhombohedron are distinguished as right and left, according to the direction in which they cause rotation of the plane of polarized light.[4]

Crystal quartz is highly transparent to ultra-violet radiation. It scratches glass readily (hardness 5–7) and becomes electrified by friction and also by heating and pressure. (Quartz is piezo-and pyro-electrically active). It is highly resistant to corrosion by various acids and alkalis and is insoluble except in hydrofluoric acid, hot concentrated phosphoric acid, and hot alkalis. Some of the more important physical constants are shown in the following:

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[1] E. F. Holden, *Amer. Mineralogist*, **8**, April, 1924.

[2] *Nature*, Nov. 8, 1924.

[3] M. L. Huggins, "The Crystal Structure of Quartz," *Phys. Rev.*

[4] J. A. Audley, Silica and the Silicates.

SOME PHYSICAL CONSTANTS OF α QUARTZ

Specific gravity*		2.646
Sp. volume cc./g.*		.3779
Thermal conductivity in gram calories*		
Parallel to axis		.0325
Perpendicular to axis		.0586
Linear expansion*		
Parallel to axis (t, 0–80°)	C x 10^4 = .1337 or	.00001337
Perpendicular to axis (t, 0–80°)	C x 10^4 = .0797	.00000797
Cubical expansion (t, 0–100)	C x 10^4 = .3840	.00003840
Specific heat (t, 12–100) g. calories		.188
Index of refraction*		
Wave length .396μ		1.55815
Wave length .760μ		1.53917

Transmissibility to Radiation

Quartz is transparent to ultra-violet. Pfluger gives transmission values for a plate 1 cm. thick as follows:

.222μ	94.2%*
.214	92.0
.203	83.6
.186	67.2

C. P. Goertz states that crystal quartz has the same transmission as fused quartz for radiation in the region between 450 and 300 millionths mm. (4500 to 3000 Å). George Joos reports[1] as the result of some experiments on the transmission of the copper spectrum through clear and crystal quartz plates of 6 mm. thickness, that absorption only starts under 2000 Å and is moderate even at 1980 Å.

Crystal quartz transmits radiation in the visible region of the spectrum almost perfectly.

The transmission of infra-red radiation of very long wave length is not the same in crystal quartz as in the clear fused variety.

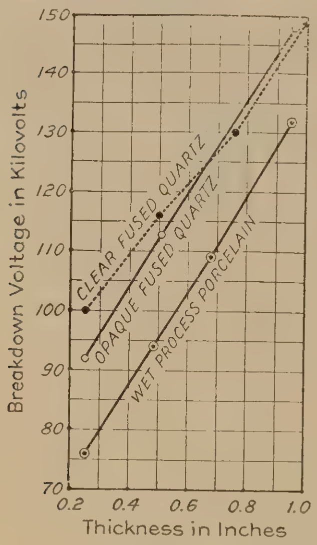

FIG. 3.—Dielectric strength of quartz and porcelain. Tests made under oil at 50°C–60 cycles–1 in. spherical electrodes. Voltage raised 1 kv. per second from 0.

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* Smithsonian Institution.

[1] G. Joos, *Phys. Zeit.*, **25** [15], 374–76 (1924).

Crystal quartz is opaque to radiation of 7μ, (70000 Å or .007 mm.) at 8.50μ metallic reflection occurs. At wave length 24.4μ it is again transparent. At wave length 108μ crystal quartz is transparent whereas the clear fused variety is completely opaque.[1]

The specific inductive capacity is not the same in all directions in a crystal. It depends upon the direction of the plane to the optic axis. For wave lengths greater than 10,000 cm. the specific inductive capacity,[1] parallel to axis = 4.69 and[1] perpendicular to axis = 5.06.

Transformation of Crystal Quartz The alpha quartz discussed in the preceding is apparently stable at temperatures below 575°C. When brought to this temperature it changes its physical properties, entering the β state. The constants for the β state have not been determined; however, the transformation is marked by a sudden volumetric change which breaks the crystal into a great number of pieces.

The transformation is reversible and very sensitive. A variation of 0.1°C is sufficient to determine the change from α to β. The reverse transformation of β to α does not occur at 575°C but 5° lower at 570°C. The density of β quartz is thought to be 2.633.[2]

Tridymite

Tridymite is a crystallized variety of silica found in minute transparent tabular hexagonal crystals in tachyte and other igneous rocks, usually in twinned groups, and commonly of three crystals. It also occurs in plates of hexagonal shape consisting of agglomerations of biaxial orthorhombic crystals.

It is thought that there are three forms of tridymite. The α tridymite changes to β_1 tridymite at 117°C, the temperature of transformation. At 163°C, β_1 tridymite changes to β_2 tridymite. The transformations are reversible.

Tridymite is soluble in hydrochloric acid and in boiling sodium carbonate.[3] Some of its physical constants follow:[2]

Specific gravity α form	2.28
Index of refraction (D_1) 0.469 to	1.473
Melting point	1670°C

Tridymite is easily produced by heating crystal quartz sand in the presence of "mineralizing" agents (as chloride of potassium or lithium) at between 800° and 1500°C. It is also produced (with cristobalite) in the absence of "mineralizing" agents when crystal quartz sand is heated in the electric furnace for a short time at near the point of fusion (about 1700°C).[1]

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[1] Smithsonian Institution.

[2] G. Flusin, "Le Verre de Silice," *Chem. et Industrie.*

[3] Century Dictionary.

Fused quartz heated in the presence of a suitable catalyst such as chloride of potassium or lithium, devitrifies at comparatively low temperatures; thus, continuous heating for eight days at 800°C converts vitreous silica into tridymite.[2]

Cristobalite

This variety of silica has at least two forms, called α and β. The α cristobalite is found in small octohedric crystals. The β cristobalite crystals are cubical. The transition point is variable.[3]

If the cristobalite has been formed at 1600°C the transition point is 270°C on heating, and 230°C on cooling. It diminishes to as low as 220° and 200°C and depends upon the magnitude of the previous highest heating temperature.[4]

Cristobalite is formed by heating precipitated silica at 1000°C. Both crystal quartz and fused quartz are transformed to cristobalite by heating at 1000°C. The speed of reaction is a function of the temperature, grain size, time of heating, and purity of the silica.

"Devitrification scarcely commences at 1120°C but is appreciable after four hours of continuous heating at 1140°C."[2]

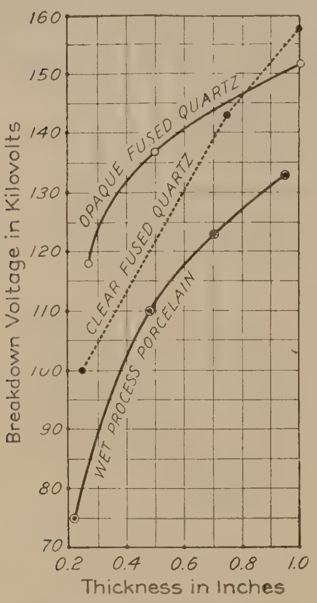

FIG. 4.—Dielectric strength of quartz and porcelain. Tests made under oil at 100°C–60 cycles–1 in. spherical electrodes. Voltage raised 1 kv. per second from 0.

The specific gravity of cristobalite[4]	=2.32
The melting point is about	1700°C
Ferguson and Merwin[5]	1710°C
Rudolph Wietzel[4]	1696°C
Index of refraction[6] (D_1) 1.484 to	1.487

Transformation of Crystalline Silica

The three crystalline varieties of silica can be transformed from one form to another by heating at 870°C.[6] The speed of reaction is very slow but increases with increase of temperature. The mechanism determining these transformations is imperfectly understood.

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[1] Thomson Research Lab., G. E. Co., H. L. Watson.

[2] Richard Paget, *loc. cit.*

[3] Fenner, *Z. Anorg. Chem.*, **85**, 133 (1914).

[4] R. Wietzel, The Equilibrium Relations of Fused and Crystal Phases of SiO_2.

[5] Ferguson and Merwin, *Amer. Jour. Sci.*, **45**, 322 (1918).

[6] G. Flusin, *loc. cit.*

Cryptocrystalline Forms of Silica

The cryptocrystalline forms of silica are generally physically hydrated. Specimens consist of agglomerations of microscopic particles of anhydrous silica separated by ultramicroscopic spaces (diameter of the order of 1.1 x 10^{-5} mm.) filled with water.[1]

The cryptocrystalline varieties are named according to color or structure. The following belong in this class:[2]

- chalcedony
- onyx
- sardonyx
- carnelian
- heliotrope
- agatized wood
- agate (in many forms)
- prase
- chrysoprase
- flint
- hornstone
- jasper
- basanite

Natural Hydrated Amorphous Forms

Opal and tripoli do not show, even under the microscope, evidence of crystallization and are generally considered amorphous. Various forms of opal have specific gravity of 1.9 and 2.3, and contain from 3 to 9% of water. There are many varieties as: (*a*) precious or noble opal (including the harlequin opal) with brilliant and changeable reflections of green, yellow, and red; (*b*) the fire opal, which affords an internal red fire-like reflection; (*c*) common opal, whose colors are white, green, yellow, and red but without the play of colors; (*d*) semiopal, the varieties of which are more opaque than common opal; (*e*) hydrophane, which is transparent only when immersed in water; (*f*) hyalite, which occurs in small globular and botryoidal forms, colorless and transparent with vitreous luster; (*g*) menilite, which occurs in irregular or reniform masses and is opaque or translucent; (*h*) and fiorite, siliceous sinter, or geyserite, the form of silica deposited by hot springs and geysers.

The production of artificial hydrated forms of silica of the opal type seems not to have attracted the attention of experimenters.

Tripoli or tripolite, the second hydrated amorphous type of silica, called infusorial earth, is formed of the siliceous shells of diatoms.

Artificial Hydrated Amorphous Silica

Chemically precipitated silica (SiO_2) is the only amorphous hydrated type that has been so far produced. When first precipitated it contains 90% of water. This can be reduced to about 3% by drying.

Precipitated silica changes gradually to cristobalite when heated at 1000°C.

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[1] G. Flusin, *loc. cit.*

[2] Century Dictionary

Fused Quartz
Amorphous Anhydrous Silica

All crystalline forms of silica are transformed at sufficiently high temperatures into an amorphous anhydrous product, which may be clear, opaque, or translucent, and which has important physical properties.

The fusion of clear quartz intended for optical purposes requires the careful selection of crystals free from inclusions. Quartz crystals may contain microscopic drops of water, carbonic acid, sodium chloride, and small particles of glass. Crystals of different origin produce different results in fusion. Helberger states as the result of tests made on crystals from various sources, that material obtained from Gotthard and Brazil was found most suitable.[1]

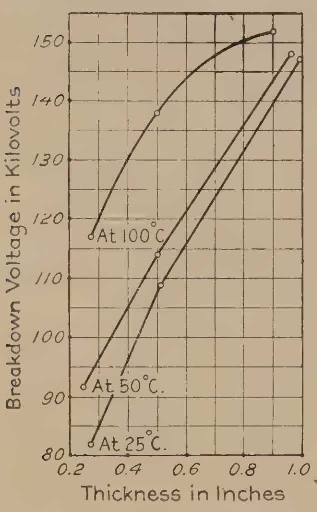

FIG. 5.—Dielectric strength of opaque fused quartz.

When crystal quartz or quartz sand is heated at a temperature above 1000°C it changes more or less rapidly into cristobalite and tridymite, if the temperature is not permitted to increase beyond 1700°C. However, by rapidly elevating the temperature to beyond 1700°C, the material is made to enter the vitreous state. If heating proceeds too slowly, quartz, which has begun to fuse, may be transformed into solid cristobalite or tridymite, which is then fusible at higher temperatures.

The transformation of quartz into the amorphous anhydrous product begins at 1470°C. The first signs of softening appear at 1650°C. It enters into plastic fusion at between 1750° and 1800°C.

The volatilization of silica begins at about 1650°C, except in the presence of carbon or hydrogen where it begins at 1250°C. In the latter case there is really a partial reduction and sublimation rather than pure vaporization. At 1800°C volatilization is very pronounced. The following data indicates the general order of magnitude of this effect (translucent quartz fusion).

Run	Temp °C	Time*	Loss %
1	1800	5 min.	1.0
2	2000	" "	20.5
3	2200	" "	38.3

The evaporation of silica in the production of clear quartz has a minimum of over 30%.[2]

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[1] H. Helberger, *Zeits. fur Tech. Phys.*, 5, No. 10.

[2] Thomson Research Lab., G. E. Co., H. L. Watson.

* Time held at maximum temp.

The silica does not become fluid at 1800°C, but only soft and plastic. However, if the temperature is rapidly increased to between 2000° and 2500°C the viscosity is considerably reduced so that the mass can be poured. These important temperatures can be tabulated as follows:

Formation of β quartz	575°C
Sublimes in presence of H or C	1250°C
Change to vitreous form starts	1470°
Begins to soften	1650°
Enters state of plastic fusion	1750°
Fused quartz is fluid above	2000°

At about 1400°C the small content of impurities which exists in amounts of about 0.2% in the purest silica (sand) commercially obtainable, will begin to show signs of weak fluxing activity and the mass will begin to cohere, even though the temperature is at least 450° below the theoretical melting point of pure silica.[1]

Latent Heat of Fusion of Quartz The latent heat of fusion of vitreous silica has not been experimentally determined. Calculated values (Richard) (Vogt) indicate[2] it is about 64 to 66 gram calories per gram. It is, however, known that vitreous silica does not restore the heat of fusion in cooling; consequently fused quartz at low temperatures can be considered a liquid of extreme viscosity.

Physical Properties of Fused Quartz A considerable mass of data has been accumulated indicating values for the more common properties of the amorphous anhydrous form of silica.

In the following, the word "translucent" refers to that variety of fused SiO_2 produced by the fusion of silica sand. This product is translucent except in large masses.

Specific gravity varies with homogeneity

[3]Translucent fused quartz	2 to 2.1
[3]Clear fused quartz	2.21 to 2.213

Thermal expansion (linear)

[2]Clear fused quartz t, 0–100°C, 49 x 10^{-8}

[4] " " " t, –190– 16, C x 10^4 = –0.0026

[4] " " " t, 16–500, C x 10^4 = 0.0057

[4] " " " t, 16–1000, C x 10^4 = 0.0058

[5]Translucent fused quartz t, about 25°C = .00000059

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[1] J. Scharl and W. Savage, Commercial Development of Fused Silica.

[2] G. Flusin, *loc. cit.*

[3] Thomson Lab., G. E. Co.

[4] Smithsonian Institution.

[5] The Thermal Syndicate, Ltd.

Linear expansion determined using fused quartz tube fused onto fused quartz interferometer plates[1]

t,	26–83°C	58×10^{-8}
t,	83–177,	66×10^{-8}
t,	177–269,	66×10^{-8}
t,	26–966,	55×10^{-8}

Thermal expansion (cubical)

[1] Clear fused quartz *t*, 0–80C, 129×10^{-8}

The thermal expansion of glass of the more common types is 12 to 18 times that of pure fused quartz.

Specific heat, g. calories per g.

[2]*t*,	100°C	.204
[2]*t*,	500	.266
[2]*t*,	1000	.290

Mean specific heat

[3]*t*,	0–100	.1845
[3]*t*,	0–500	.2302
[3]*t*,	0–900	.2512

[2]Latent heat of fusion

64 to 66 g. calories per g.

Thermal conductivity g. calories per second per cc. per °C

[2]Translucent fused quartz		.002
[3]Clear fused quartz (sp. gr. 2.17)	(*t* 20°C)	.00237
	(*t* 100)	.00255

Hardness

[2]Silica glass (Mohs scale) 4.9

Fused quartz is harder than opal, [4] and some glasses, but softer than crystal quartz 5. 7, and hard (crown) glass, 6.2.

Volumetric Changes of Transformation of Crystallized to Vitreous Silica

[2]Quartz	to vit. silica	20. % increase in volume
[2]Tridymite	" " "	3.1 % increase in volume
[2]Cristobalite	" " "	5.4 % increase in volume

Permeability of Fused Quartz to Gases Fused quartz at normal atmospheric temperatures and at low pressures is impermeable to gases. At higher temperatures it is permeable to certain gases.

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[1] Bur. Standards.

[2] G. Flusin, *loc. cit.*

[3] Smithsonian Institute.

[1]Hydrogen diffuses		at 1000°C
Methane	diffuse	at 1300°C
Nitrogen		
[1]Oxygen		
[1]Helium	diffuses	at 300°C

[2]Hydrogen diffuses at 56 cm. pressure at 330°C
[2]N and O begin to diffuse at atm. pressure at 430°C

At temperatures between 700° and 1000°C the solubility of hydrogen in fused quartz is of the same order as that of hydrogen in water at 20°C, *i.e.*, .00160 g. per kg. at 760 mm. pressure.[3]

Chemical Properties of Fused Quartz

Acids Fused quartz is insoluble in all acids except phosphoric and hydrofluoric. Phosphoric acid combines with silica producing silicon phosphate.[3] Hydrofluoric acid combines producing fluoride of silicon or fluosilicic acid.

Comparative values indicating the speed of reactivity of hydrofluoric acid with various substances including fused quartz[2]:

Ordinary glass	1000
Fused quartz	100
Quartz parallel to axis	11
Quartz perpendicular to axis	1

Bases Fused quartz or vitreous silica is soluble in aqueous solutions of strong bases, as lithium, sodium, potassium, thallium, barium, strontium, calcium, and ammonium hydroxides; and in general in salts producing alkaline reactions. At ordinary temperatures the speed of reaction is so small as to generally escape observation. The speed of reaction rapidly increases with the temperature but depends also on time and concentration of the solvent. The following data[2] indicate the general order of reactivity of vitreous silica with various alkaline substances.

Temperature 18°C
90 sq. cm. SiO_2 in contact with reagent

Time (days)	Reagent	Concentration	Loss mm. gr.
2	$NH_4(OH)$	10%	.8
2	NaOH	10%	.4
2	KOH	30%	1.2

---

[1] L. V. Hirschberg, *Zeits. für angewandte Chem.* (Berlin-Pankow).
[2] G. Flusin, *loc. cit.*
[3] Smithsonian Institution.

Time (days)	Reagent	Concentration	Loss mm. gr.
14	Na_2CO_3	1/N	.6
14	$Ba(OH)_2$	saturated	0.0
14	$Na(HPO)_7$	"	0.0
At 100°C			
Hours			
3	NaOH	2/N	33.0
"	KOH	2/N	31.0
"	Na_2CO_3	2/N	10.0

At high temperatures fused quartz is attacked by metals of the alkaline earth group. Tubes of fused quartz wound with nichrome wire are rapidly attacked at 900° to 1000°C. Silica is attacked by oxides of metals (at temperatures above 900°C) such as those of calcium and copper.

Annealing Fused Quartz

An examination in polarized light of clear fused quartz disks approximately 2 cm. thick and 7.5 cms. in diameter indicated that the specimens were highly strained.

Temperatures chosen for annealing tests on these samples were 1045°, 1070°, 1090°, and 1120°C. The annealing period was 2 hours. The cooling rate was started at 20°C per hour and increased so that samples could be removed from the furnace about 10 hours later.

After none of these treatments, with the possible exception of that of 1070°C was there a noticeable diminution in the strain evident by examination in polarized light. If any change occurred after treating at temperatures of 1090° and 1120°C these rough tests in polarized light indicated an increase in the strain.

"If strain results chiefly from inhomogeneities in the original crystals or differences between them before being fused together, no amount of ordinary annealing will reduce it. If the strain and inhomogeneity results from a tendency of the molecules while the glass is cooling through certain temperature ranges to reassume their alignment in the original crystals, then treatments which involve only low annealing temperatures and extremely rapid cooling through such ranges may aid in preventing these defects."[1]

Electrical Properties of Clear and Translucent Fused Quartz

The resistance of fused quartz is of the electrolytic order and consequently decreases with increase of temperature. At normal temperatures the volumetric resistance is of the order of 10^{19} of ohms per cm^3. The following tabulation indicates the specific resistance at various temperatures of both the clear and translucent varieties.

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[1] Bur. Standards.

Ohms/cc. (volumetric resistivity)

Temperatures	Ohms	Temperatures	Ohms
[5]15°C (above)	4×10^{18}	[1]700	30×10^{6}
[2]25 (above)	1×10^{19}	[1](800)	(20×10^{6})
[1](150)	(2×10^{14})	[4](800)	(20×10^{6})
[3](150)	(2×10^{14})	[3](800)	(20×10^{6})
[1]230	2×10^{13}	[2]1800	2134
[1]250	25×10^{11}	[2]1950	189

[1]Ordinary glass is liquid at 1600°C, the resistivity being of the order of 0.1 ohm/cm^3. Porcelain at 25°C has resistivity of 1×10^{14} ohms/cm^3. which compares[2] to fused quartz at about 200°C.

Surface Leakage of Fused Quartz

Moisture does not condense on the surface of fused quartz in damp atmospheres; consequently it does not acquire the surface conductivity common with some insulation under similar circumstances.

The following data obtained at 25°C indicates leakage in amperes per cm. length at 500 volts d.c. with 1 cm. spacing between electrodes; of specimens of fused quartz and porcelain.

[2]At 50% humidity

Translucent fused quartz	(6 specimens)	2.1×10^{-11} to 6.7×10^{-12} amp.
Porcelain	(3 specimens)	5×10^{-11} to 7×10^{-12} amp.

[2]At 90% humidity

Translucent fused quartz	(6 specimens)	1.1×10^{-7} to 1.9×10^{-9} amp.
Porcelain	(3 specimens)	1×10^{-6} to 2×10^{-6} amp.

Dielectric Strength

The dielectric strength of fused quartz varies with the thickness of samples tested. In thin plates values have been obtained greater than 500 volts per mil.[6] The dielectric strength varies with the temperature. Tests of specimens under oil between 1 in. spherical electrodes, at various temperatures, produced the following results:[2]

Translucent fused quartz approximately $\frac{1}{4}$ in. thick.

Temp.	No. of breaks	Av. volts/mil.
25	8	298
50	7	410
100	5	397

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[1] G. Flusin, *loc. cit.*

[2] General Engineering Lab., G. E. Co.

[3] Natl. Phys. Lab. (London).

[4] L. V. Hirschberg, *loc. cit.*

[5] Bur. Stand.

[6] Singer, Die Keramik, p. 297 (Braunschweig, 1923).

Translucent fused quartz approximately ½ in. thick

Temp.	No. of breaks	Av. volts/mil.
25	6	203
50	4	230
100	5	238

Translucent fused quartz approximately ¾ in. thick

Temp.	No. of breaks	Av. volts/mil.
25	5	161
50	3	174
100	4	190

Translucent fused quartz approximately 1 in. thick

Temp.	No. of breaks	Av. volts/mil.
25	3	144
50	1	149
100	2	159

Tests made on porcelain at the same time the above data was obtained indicate that the dielectric strength of this material is considerably less than that of fused quartz at the same temperatures. Values tabulated for the dielectric strength of fused quartz are approximately 20% greater for ¼ in. material and 10% greater for 1 in. material than those obtained for wet process porcelain at 25°, 50°, and 100°C. Tests have been made that indicate that clear and opaque fused quartz specimens of similar form and under similar conditions have about the same values of dielectric strength at the same temperatures.

Dielectric Constant of Fused Quartz

Constant	Frequency	Authority
3.7		Bur. Stand.
3.5 to 3.6		Singer, *loc. cit.*
4.4	100,000	General Eng. Lab., G. E. Co.

The value 4.4 was obtained for a specimen of opaque quartz ¼ in. thick and 5 in. diameter, at 25°C, 60% humidity.

Dielectric Losses in Fused Quartz and Other Insulation

An insulating material of high resistivity and of great dielectric strength may be useless at high frequencies if it has high dielectric losses.

As shown in the following tabulation of data, the dielectric loss in fused quartz is less than in most comparable materials.

*Power losses in dielectrics.

(Temp. approx. 25°C)	C x 10^6
[1]Translucent fused quartz	0.57
[2]Clear fused quartz	0.94
Mica	0.47– 1.13
Paraffin	0.85– 3.02
Rosin	2.65
Porcelain	20.00– 30.00
Glass	10.00– 23.50
Bakelite	80.00–110.00
Pressboard	66.00
Rubber	77.50
Enamel of wire insulation	33.00

* The dielectric losses are proportional to a characteristic coefficient of the material, to the frequency and to the square of the electric field, or,

$W = CF^2f$, where,
W = the power loss per unit volume, watts/cm^3.
F = the electric field, kilovolts/cm.
f = the frequency in kilocycles.

Phase Difference, Power Factor, Loss Factor

Tests made on a specimen of translucent fused quartz 5 in. diameter and $\frac{1}{4}$ in. thick resulted in the following values:[1]

Power factor (%)	K	Loss factor
0.13	4.4	0.57

K = dielectric constant.

The phase angle of a specimen of clear fused quartz was found to be less than 20 seconds, this value being the limit of the measuring apparatus.[3] Some comparative tests made on specimens of clear and translucent fused quartz resulted in data indicating that the clear variety has a higher power factor than the translucent; furthermore, the clear specimens tested varied in value of power factor obtained, in a series of tests covering a period of several weeks, from 0.43 to 0.21%. The translucent specimen was $6\frac{1}{4}$ in. diameter and $\frac{1}{4}$ in. thick. The clear specimen measured 8 in. x $7\frac{1}{2}$ x $\frac{1}{8}$ in. thick. Data obtained follows:

	Date	PF (%)	K	PF×K
Translucent	Nov. 21, '24	0.13	4.4	0.57
“	“ 29, “	0.13	4.4	0.57
“	Dec. 1, “	0.13	4.4	0.57
Clear	Oct. 9, “	0.43	4.5	1.94
“	Nov. 24, “	0.29	4.2	1.22
“	“ 25, “	0.27	4.2	1.13
“	“ 26, “	0.23	4.2	0.97
“	“ 28, “	0.23	4.2	0.97
“	“ 29, “	0.23	4.2	0.97
“	Dec. 1, “	0.21	4.2	0.88

PF = power factor. See definition in Supplement.
K = dielectric constant
PF×K = loss factor

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[1] Gen. Eng. Lab., G. E. Co.

[2] P. Bouvier, *Radio Electricite*, 5 [51] (1924).

[3] Bur. Standards.

Tests were made at 100 kilocycles, 60% humidity, 25%C.

Mechanical Properties of Fused Quartz

Ultimate Strength in Compression

The end conditions of test specimens greatly affect the crushing strength of fused quartz. Tests in which soft sheet lead, paper, paraffin, and vaseline were used to cause uniform distribution of pressure, indicated that vaseline was the most effective of substances tried. "In the case of vaselined ends the failure was accompanied by a loud report and complete disintegration of the specimen into fine powder. With other materials the specimens were broken into large fragments. A specimen which withstood a lower load would break into fragments fewer and larger than the fragments from the specimens which withstood higher loads."[1]

In the following tabulation the lower values were obtained on specimens whose flat ends were not exactly parallel; the difference in the length of any specimen at different places being as much as .002 in. The length of test specimens was 1.5 in.; the ends were vaselined; the diameters varied from .397 to .547 in.

Specimen	Ultimate Strength (lbs./sq. in.)	Specimen	Ultimate Strength (lbs./sq. in.)
1 (diam. .547 in.)	191000	4 (diam. .510 in.)	148000
2 (diam. .509 in.)	154000	5 (diam. .510 in.)	114000
3 (diam. .508 in.)	156000	6 (diam. .397 in.)	97000

The compressive strength of fused quartz is probably greater than 191000 lbs./sq. in., the largest observed value. It is 3 or 4 times that of hard porcelain. Some comparative values follow:

Specimen	Ultimate Strength (lbs./sq. in.)
[2]Granite	20200
[2]Marble	12600
[2]Limestone	9000
[2]Sandstone	12500
[3]Hard porcelain	56300

The modulus of elasticity of fused quartz in compression is about 9400000 lbs./sq. in. (Determined by optical extensometer.)[1]

Ultimate Strength in Tension

Values for tensile strength of fused quartz tabulated in the following were obtained with the ends of specimens roughened with emery powder and inserted into closely fitting brass tubes filled with De Khotinsky cement. In order to apply an axial load to specimens, thin steel strips were secured in slots in the outer end of each tube, so that the load caused tension in the strip. The strip was carefully centered with the axis of the specimen. Pins which passed through holes in the outer end of each strip were loaded by the testing machine. As the line connecting the centers of the two holes coincided with the axis of the specimen, the loading was nearly axial.

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[1] Bur. Standards.

[2] Smithsonian Institution.

[3] Singer, *loc. cit.*

"It will be noted that the observed tensile strength decreases with increase in the diameter of the test specimen. This is probably due to the effect of non-uniform loading of specimen, which is becoming more and more difficult to obtain with the increase of the diameter of specimen."[1]

Specimen	Diameter	Tensile strength lbs./sq. in.
Clear	0.250 in.	6950
"	.343	3290
Opaque	.392	2650
"	.398	1610

Modulus of Rupture in Torsion

The following values listed for the torsional strength of fused quartz were obtained using an Amsler-Laffon torsion machine of 15 m. kg. (109 ft.-lb.) capacity reading to 0.001 m.k. (0.07 ft.-lb.) Sealing wax was used to hold the specimens in cylindrical holders.

Specimen	Diameter	Length of specimens between holders	Modulus og rupture lbs./sq. in.
Clear	0.565 in.	3.69 in.	6760
"	.544	3.00	6870
Opaque	.405	10.00	2300

Transverse Strength of Fused Quartz

Transverse tests on fused quartz specimens were made under conditions of a single beam loaded at two points in the middle.[1]

"Steel blocks 0.25 in. long, fitting the cylindrical surface of specimens were used at the supports and for applying load. The supporting blocks were resting on the knife edges and the load was transmitted to the loading blocks also through knife edges. The surface of specimen in contact with the loading and supporting blocks was covered with grease. These and other precautions taken were apparently sufficient to secure a proper distribution of load, as all of the tested specimens broke near the middle of the specimen and the appearance of the fracture was very similar in all cases." The deflection was measured by a dial reading by estimation to 0.0001 in.

Values listed in the tabulation for the modulus of rupture and modulus of elasticity were computed using the formulas stated in the following:

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[1] Bur. Standards.

[1]Modulus of rupture $= \frac{Pda}{4I}$

[1]Modulus of elasticity $= \frac{P/I}{L} \times \frac{a(3 \times l^2 - 4a^2)}{48}$

where,
P = the total load (lbs.)
d = diam. of specimen (in.)
I = moment of inertia of cross section (in.^{4})
L = deflection in the middle (in.)
l = distance between the supports (5.5 in.)
a = distance from the point of application of load to the support (1.75 in.)

Specimen	Diameter	Mod. R*	Mod. E*
Clear	.575	10800	12660000
"	.455	9480	10550000
"	.507	9180	10330000
"	.503	8410	11840000
"	.561	7070	10840000
Opaque	.387	5390	11400000

* Mod. R = Modulus of rupture lbs./sq. in.
Mod. E = Modulus of elasticity lbs./sq. in.

The higher values shown in the preceding tabulation were obtained for unground specimens.

Optical Properties of Clear Fused Quartz
Transmissibility to Radiation

Clear or transparent fused quartz is very transparent to ultra-violet radiation of wave lengths longer than 0.193 μ.[2]

In some experiments on the absorption of ultra-violet radiation in fused quartz specimens of various thicknesses, it was determined that 1 inch of this material will transmit perfectly radiation as low as 2300 Å units; four inches of fused quartz transmits as low as 2500 Å and absorbs radiation of shorter wave length; 8 inches has for its lower limit the line 2536 Å and 11 inches stops all radiation below 2650 Å units.[3]

A fused quartz mercury arc lamp, grating spectroscope, and accessory apparatus were used in tests resulting in data given in the following tabulation. Special plates were not used.

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[1] Bur. Stand.

[2] G. Flusin, *loc. cit.*
Singer, *loc. cit.*
Phys. Zeit., **25** [15] 374–76 (1924).

[3] Thomson Research Lab., G. E. Co.

Absorption of Ultra-violet in Fused Quartz

Length of specimen	Exposure in seconds	Lowest line identified (in angstrom units)
0	35 sec. (*)	2299[1]
1	"	2299
$2\frac{7}{8}$	"	2464
$3\frac{15}{16}$	"	2464
$7\frac{7}{8}$	"	2536
$10\frac{7}{8}$	"	2657

(*) Lowest line identified through air only.

M. von Schwartz has stated as his conclusion, resulting from consideration of measurements made by George Joos, that only fused quartz produced by Hugo Helberger's process is capable of passing ultra-violet radiation of short wave length, presumably below 2400 Å units.[2] However, George Joos reports his belief that the negative results of other experimenters in measurements of the transmission characteristics of fused quartz at low wave lengths, may be due to a discontinuity in the spectrum of the quartz mercury lamp.[3] It is also apparent that the type of photographic plate employed is important.

In the literature among quantitative measurements are those of Pfluger, that a plate 2.81 mm. thick passed only 56% at 2100 Å and none under 2000 Å. However, in some experiments on the transmission characteristics of fused quartz, George Joos photographed the copper spectrum through fused quartz plates 6 mm. thick and obtained results indicating no absorption above 2000 Å and only moderate absorption at 1980 Å. Halbschuhman photographic plates made according to van Angerers directions were used.

Flusin[4] states that absorption is complete at 1930 Å but does not give the conditions of his experiment.

Clear fused quartz is completely opaque to infra-red radiation of 108 μ wave length, whereas silica in the crystal form is transparent.[5]

Specimen	Thickness (cm.)	Wave Length	Transmission (%)
Clear fused quartz	3.85	108μ	0
Parallel to axis	2.00	"	62
Transverse to axis	2.00	"	81

Refraction and Dispersion

The index of refraction of fused quartz at wave lengths corresponding to the position of the Fraunhofer lines *D*, *C*, and *F* is,[4]

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[1] H. P. Hollnagel, Thomson Research Lab., G. E. Co.

[2] M. von Schwartz, "Fused Quartz Free of Bubbles," *Phys. Zeits.*, Aug. 1, 1924.

[3] G. Joos, "The Transparencey of Quartz Glass," *Phys. Zeits.*

[4] G. Flusin, *loc. cit.*

[5] Smithsonian Institution.

Index	Line	Wave Length
1.4585	*D* (Na)	5896.155 Å
1.55093	*C* (H)	6563.045
1.55899	*F* (H)	4861.527

The mean dispersion is therefore $1.55899 - 1.55093 = .00806$, and the optical constringence, $1.4585 - 1/.00806 = 56.8$. Tabulating we have,

Index of refraction Na line D.	1.4585
Mean dispersion	.00806
Optical constringence	56.8

The Comparative Values of Fused Quartz and Porcelain in the Construction of Electrical Insulation

Fused quartz and porcelain are similar in that they are slowly attacked by basic reagents but insoluble in nearly all acids. Both are attacked at high temperatures by metals of the alkaline earth group and by oxides of metals. Both materials are very resistant to abrasion and corrosion by exposure to weathering influences. They are not easily reduced in the presence of carbon or reducing gases even at temperatures near their softening points.

As indicated in the preceding tabulation of data the resistance of one centimeter cross-section of fused quartz 1 centimeter long, is equal to that of 1 centimeter cross-section of porcelain 1000 meters long, *i.e.*, the resistivity of fused quartz is 100,000 times that of porcelain, (at 25°C).

Fused quartz has at least five times the specific resistance of new hard rubber, which material has been recommended for years as the most satisfactory substance obtainable for use in the construction of low loss apparatus in radio engineering. Some comparative values follow:

Specimen	Volume Resistivity Megohms–cms.	Specimen	Volume Resistivity Megohms–cms.[2]
Fused quartz (above)	5 x 10^{12}	Rosin	5 x 10^{10}
New hard rubber	1 x 10^{12}	Paraffin	1 x 10^{10}
Clear mica	2 x 10^{11}	Shellac	1 x 10^{10}
Sulphur	1 x 10^{11}	Porcelain	3 x 10^{8}
Amber	5 x 10^{10}		

The dielectric strength of fused quartz at temperatures between 25° and 100°C is from 10 to 20% greater than that of porcelain under the same conditions. As has been shown the dielectric strength of fused quartz may reach 500 volts per mil. (in thin plates). However, purified asphalt in thin films (0.5 mm.) has dielectric strength of 2400

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[1] Smithsonian Institution.

volts per mil.[1] Bengal mica has dielectric strength in plates 0.1 mm. thick as high as 5000 volts per mil.[2]

As has been shown in the preceding, the dielectric losses in fused quartz are lower than in most comparable materials.

The best known property of fused quartz is its great resistance to thermal shock. This is, of course, due to the very low coefficient of thermal expansion. At temperatures between 0° and 1000°C it is less than that of any other known substance, The linear expansion of porcelain is about 0.3×10^{-5}; more than 10 times that of fused quartz. Since electrical insulation may be exposed to thermal changes and thermal shocks of considerable magnitude it is apparent that fused quartz should provide better performance than any other ceramic material in this service.

The mechanical strength of fused quartz in torsion and tension compares with that of other ceramics.[3] In compression, the ultimate strength under favorable conditions is many times that of other ceramics. The material, however, is nearly as brittle as glass, and is greatly affected by small variations in conditions of loading.

Conclusions

Fused quartz has greater electric resistance than any other known substance at equivalent temperatures. It has lower thermal expansion than any other insulation, and consequently has greater resistance to thermal shock than porcelain or other ceramics. The compressive strength is greater than that of any comparable substance, (the material is, however, brittle and glass-like; consequently the maximum strength can probably not be utilized in practice). It is non-hygroscopic and furthermore highly resistant to corrosion and abrasion.

Both clear and translucent fused quartz are essentially homogeneous and uniform materials. The qualities enumerated in the preceding are very constant.

No damage results (to insulators) in the case of over-voltage surges on lines protected by fused quartz insulation. "The heat of an arc playing over its surface neither makes it a conductor nor splinters it."[4]

This property of resistance to intense electrical discharges is the result of the combination of the several peculiar physical properties of this material in one substance. The high melting point prevents change of form through the application of high temperatures for short periods of time. High internal radiation causes the dissipation and distribution of heat applied at one point. The low expansion provides resistance to the effects of rapid temperature changes.

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[1] G. Flusin, *loc. cit.*

[2] Smithsonian Institution.

[3] High Voltage Engineering Lab., G. E. Co.

[4] Elihu Thomson, Properties of Fused Quartz.

The dielectric strength and surface leakage characteristics are such that insulation can be given a thickness sufficient to render it puncture proof for any voltage desired. In this connection it may be remarked that porcelain can be produced in sections of moderate thickness only.

In applications where the qualities enumerated in the preceding are important, fused quartz is the best material available for electric insulation.

From the preceding data, it is evident that silicon-dioxide possesses some very unusual properties, among which may be mentioned: the piezo-electric effect of the crystalline variety, high transmission of ultra-violet light as applied to the mercury vapor lamp, and the low losses of translucent fused quartz at high frequency. A careful examination of the fused quartz varieties discloses many unique properties, and it is felt that a detailed study of these data will result in a wide field of application and utility.

Supplement

Dielectric Losses in Insulation of Alternating Current Circuits

Each mass of dielectric material or insulation between conductors in every alternating current circuit functions as an electrostatic condenser. In an ideal condenser the conducting parts have zero resistance and the dielectric (insulation) has infinite resistance. On application of an alternating e.m.f. to a perfect condenser, energy will be stored by electric displacement of the dielectric while the voltage is increasing, and will be released while the voltage is decreasing. When the e.m.f. is a maximum no current will flow, and when the e.m.f. is zero the current will be a maximum. In a perfect condenser the current and voltage are therefore 90° out of phase. However, in the case of actual condensers in which material insulation is employed as the dielectric, the conditions stated above are not fulfilled. As a consequence, an alternating current flowing in an actual condenser is never exactly 90° out of phase with the impressed voltage. The difference between 90° and the actual phase angle is therefore called the "phase difference."

In an ideal condenser, as the conditions stated show, there could be no consumption of power. The existence of a phase difference consequently means a power loss, which appears as a production of heat in the condenser. The amount of the power loss, in any case, is given, as for any part of a circuit by,

$P = E\ I \cos\phi$, where,

ϕ = the phase angle between current and voltage

$\cos\phi$ = the power factor

E = the effective e.m.f.

I = the effective current.

The preceding expression is equivalent to

$P = E\ I \sin\chi$, where,

χ = the phase difference

$\sin\chi$ = the power factor.

The phase difference is small except in the case of very poor insulation; therefore, $\sin\chi = \chi$ and the phase difference and power factor are synonymous. The power loss in a condenser is then,

$P = \omega\ C\ E^2 \sin\chi$ where,

$\omega = 2\pi \times$ frequency

C = electrostatic capacity.

The power loss is, therefore proportional to the frequency, to the capacity, and to the power factor.

Power Factor

Insulation may cause power loss by current leakage, by brush discharge, or by the phenomenon called dielectric absorption.

When a condenser is connected to a source of e.m.f. the instantaneous charge is followed by a flow of a small and steadily decreasing current into the condenser. The instantaneous discharge of a condenser is followed by a continually decreasing current. The phenomenon is similar to viscosity in a liquid and therefore is sometimes called "dielectric viscosity."

The power factors of solid dielectrics are generally due to dielectric absorption. Dielectric absorption is, as already stated, always accompanied by a power loss which appears as a production of heat in the condenser. The existence of a power loss indicates a component of e.m.f. in phase with the current. The effect of absorption is therefore equivalent to that of a resistance either in series or in parallel with a condenser.

A resistance in a condenser in series with the capacity affects the power factor very differently from a resistance in parallel. The e.m.f. across the resistance is in phase with the current while the e.m.f. across the capacity is 90° behind it in phase. The power factor equals $\sin\chi$ and since χ is usually small it may be taken as $\tan\chi$ which is equivalent to $r\omega C$.

If $r = 1$ ohm and $C = 0.01$ microfarad, the power factor at 60 cycles $= 3.8\ (10)^{-6}$ which is entirely negligible. However, at a frequency of, for instance, 1,000,000 cycles, the power factor $= 0.063 = 6.3\%$ which is large enough to be serious.

It has, therefore, been found convenient to represent absorption in terms of series resistance. An absorbing condenser is therefore considered from this point of view and the power factor is $r\omega C$.

The power loss in an insulating material is measured by a determination of the effective resistance or equivalent series resistance of a condenser made up of the material. The measurement of resistance may be made by either the resistance variation or reactance variation method.

When the power factor is due entirely to dielectric absorption the effective resistance decreases in proportion to an increase in frequency. The variation of power factor and the equivalent resistance with frequency is a complicated matter the laws of which are not accurately known. To a first approximation, however, the power factor of an absorbing condenser is constant.

Dielectric Constant, Specific Inductive Capacity

The specific inductive capacity is the ratio of the inductive capacity of the substance to that of a standard substance and therefore is a number.

An insulator is thought to contain no free electrons. The electrons are considered bound to the molecules in such manner that they can be slightly displaced by an electric force but return to positions of equilibrium when it is removed. This motion of the bound electrons, with the electric strain in the ether itself constitutes the electric displacement in the insulator and determines its constant.

Capacity[1]

When the two conducting plates of a condenser are parallel, close together, and of large area, the capacity of the condenser is given by,

$$C = 0.0885 \times 10^{-6} \frac{K\ S}{t}, \text{ where}$$

C = microfarads
S = area of one side of one plate in cm.^{2}
t = thickness of dielectric in cm.
K = the dielectric constant (air = 1)

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[1] J. H. Morecroft, Principals of Radio Communication. Bur. Stand., *Circ.*, No. 74.

CONTINUITY IN PLASTIC BODIES[1]

By H. Spurrier

ABSTRACT

Extended experiments have shown that the plasticity of a clay increases with the growth of algae in it and the presence of hydrogel of alumina caused by a biochemical reaction. Air included in a clay body causes shortness. Experiments were run in evacuating the air in a clay and then by suddenly breaking the vacuum, collapsing the evacuated clay. The clay thus treated shows greatly increased plasticity, reduced warpage, elimination of blistering and resistance to rupture on distortion. The physics and chemistry of making clay plastic are discussed.

In presenting this contribution on the continuity of plastic bodies it may be as well to state that in an extreme sense nothing is strictly continuous. But we still refer to physical continuity in a gross sense, which implies absence of physical change as observed by our unaided senses.

Becoming interested some years ago in the physical changes wrought in plastic bodies by the mechanical processes to which they are subjected, the writer made a series of experiments, first upon the effects produced in clay bodies by pugging.

A method was developed for the determination of the amount of gases occluded in plastic bodies and the analysis of the liberated gases. The analysis of these gases showed that chemical change took place in the air occluded. Experiment was carried on with as great a continuity as other duties would permit and after about two years, the solution of the problem was found. It was discovered that under suitable conditions a specimen of clay might give off carbon dioxide and carbon monoxide almost indefinitely and that the reaction depended on a suitable supply of fresh oxygen and moisture, and finally that it was biochemical in character.

The biochemical action was found to be dependent upon algal metabolism. An attempt was made to identify the alga or algae involved. It was found that representatives of all the four main varieties of algae might occur at various times under suitable conditions: (1) cyanophyceae or blue-green algae, (2) chlorophyceae or green algae, (3) phaeophyceae or brown algae, and (4) rhodophyceae or red algae.

The most common varieties found in oxygen-fed slips were representatives of the chlorophyceae or green algae. Coincident with and probably consequently upon the growth of the algae in clay, the plasticity increases and at the same time considerable gas is evolved. If a clay slip is tested for alumina, soluble in dilute alkali, before and after the growth of algae with its consequent increase in plasticity, it will be found that more alumina is yielded to the dilute alkali in that slip in which there has occurred the greatest algal growth.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (White Wares Division.)

Assuming that the algae effected this separation of the silica and alumina, a direct experiment was made to produce the same effect in a direct and more rapid manner, the result of which was very interesting and of immediate industrial importance. For this purpose one-half per cent of hydrogel of alumina was added to a clay body which had been injured by too high a drying temperature and it was found that so small an addition immediately increased the plasticity of the clay in a marked degree.

It is known that plastic clays cannot be completely dried without some loss of plasticity and this is due largely, if not entirely, to the dehydration of the small content of hydrogel of alumina. Very commonly, a sample of plastic clay, dug moist from the earth, suffers a loss of plasticity on drying at a temperature below 100°F. Of course it is well known that the gelatinous hydrate of alumina precipitated by means of ammonia, cannot be dried without losing its gel character. Moreover it is known that long boiling makes it so gelatinous that it becomes exceedingly difficult to filter.

Physics and Chemistry of Making Clay Plastic

Shortness Due to Air Filter press cakes are usually nearly or entirely air free when fresh, but the operation of pugging invariably introduces air mechanically, more especially if the mill blades are not at the proper pitch and if the mill is not properly fed. Just dumping clay into the mill is a very sure way to injure and shorten the body by air inclusion. A pug mill should be fed in such a manner that air is not entrapped as the blades feed the clay down. This is very easy to accomplish. The great importance of this was not realized until it became possible to secure really air-free clay and if its importance were generally known, I doubt if any clay worker would ever tolerate aerated mixtures again.

To make pie-crust short, butter, lard, or some fatty substance is put in that prevents the water from knitting the particles too closely and then a lot of air is kneaded in making the body discontinuous. Precisely the same effect is produced in clay. In preparing clay for use, much more air is introduced than is usually realized and in addition during the aging of the body, more gases containing carbon dioxide are generated, which in a measure offset the good effect of the aging. Moreover, carbon dioxide has a tendency to shorten clays in other than purely physical ways.

Method of Evacuation of Air Many experiments were performed for the purpose of evacuating clay bodies, with varying success. Sometimes the body would be improved and at others it was distinctly injured and a good deal of work was done in attempt to find out the cause or causes of these varying and disconcerting results. Not much headway was made until more careful studies were undertaken, using a mercury column to determine the degree of vacuity and a volumeter to indicate initial and final volume.

By exhausting clay under kerosene, the actual air removed could be measured and it now became obvious that the expected diminution of volume was not being secured. An effort was then made to collapse the evacuated clay by suddenly breaking the vacuum and this immediately gave results that were gratifying. Subsequent experience has shown that as the degree of vacuity has increased and the vacuum break made more sudden, better results have been secured and the last inch of vacuum is found to be the most important of all.

The apparatus now being used for this purpose realizes a vacuum in daily practice within ½ to ⅝ inch of atmosphere. This is checked by a barometer. Vacuum gages have been dispensed with as entirely unreliable and only a mercury column is used to indicate the vacuum. The vacuum, after reaching within ½ inch of atmosphere, is maintained for 15 minutes and then broken suddenly (by a quick opening lever peet valve). The results are exceedingly gratifying. Benefits are secured which were quite unexpected both in nature and degree. Very extended experience has shown that in order to realize the full benefit of a highly evacuated body, it is absolutely essential to break vacuum with extreme suddenness and that the area of the vacuum break be as large as is practicable.

To this end a special vacuum break has been designed, which will open an area duly proportioned to the size of the evacuation chamber with a trigger device, which opens a plurality of ports with extreme suddenness. This device has very greatly improved the results of the operation and has presented conclusive proof that the collapsing of the evacuated vesicles by the sudden air impact is the determining factor in the process.

During evacuation it is found that there is a loss of water amounting sometimes to one-half per cent. It would be anticipated from this that the body would be a little firmer, but in practice it is found to be very considerably firmer and requires much more pressure to effect distortion, so much so that it was believed that a considerable loss of water had taken place. Repeated determinations have never shown a loss of over one-half per cent of water.

The plasticity of the evacuated product is so greatly increased, even in normally short bodies, that my veracity has been frequently questioned by those who have examined the unevacuated and evacuated material, cut from the same block of clay.

It very frequently happens that bodies formed by mechanical means suffer a distortion after forming, owing to the release of pressure and consequent readjustment of the contained air pockets.

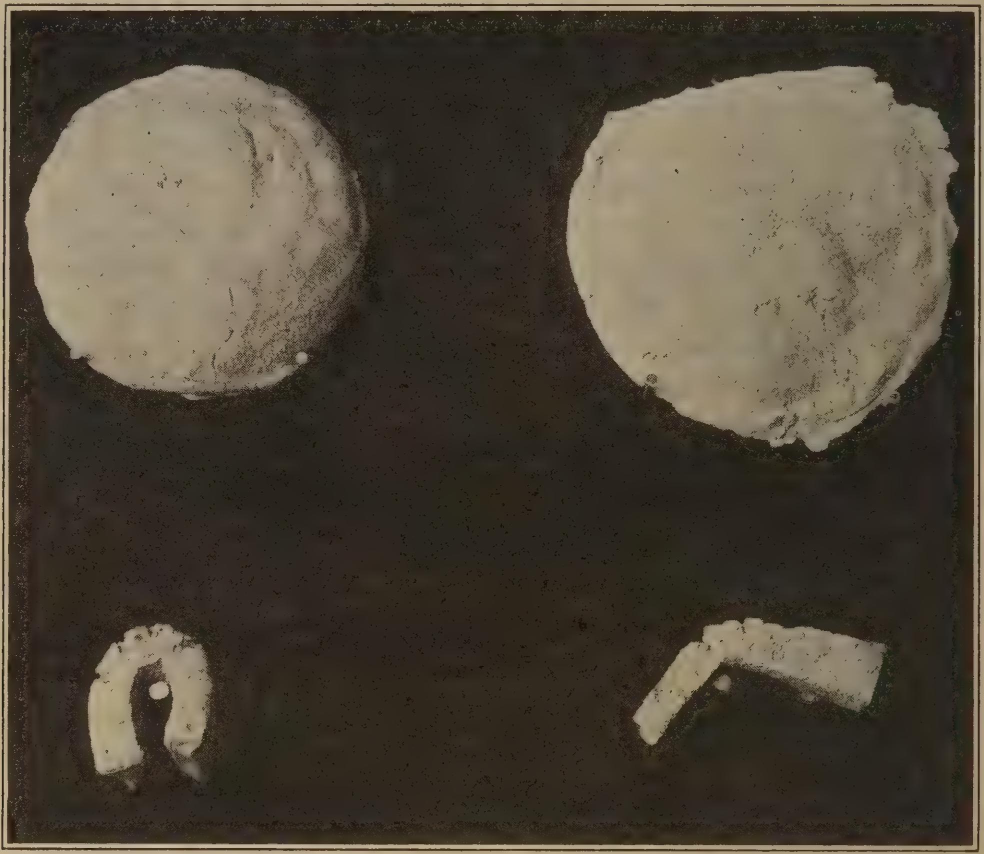

Fig. 1.—The upper part shows two balls of body referred to. That on the left is the evacuated and that on the right the untreated body after the drop test. The lower half of the photograph illustrates the two bars of body, the left being the evacuated and the right the untreated body. This piece broke at about 51° of bend; that on the left bent double or through 180° without breaking, and opened a little on drying.

It is a matter of common observation in the operation of pug mills and running out machines that the cross-section of the extruded body is noticeably greater than that of the die from which the body has been extruded, owing to the expansion of the contained air after its release from the working pressure of the mill. With evacuated clay this does not take place. Much blistering is, for obvious reasons, eliminated.

The resistance of the evacuated body to rupture on distortion is very greatly increased as will be shown by the following test:

A block of body was cut into two parts with a wire; one half was evacuated, the other being the while covered with a damp cloth. Two balls of exactly equal weight were made by approximately equal amount of handling, from the two portions of the body. The balls were then dropped from a height of 17 feet onto a smooth surface and the areas were measured by an engineer's planimeter. The evacuated piece was rounded at the edges and showed no sign of cracking at all on the periphery. The unevacuated piece flattened out to a feather edge and cracked considerably, and showed 62% greater area than the evacuated ball.

Several tests for warpage on drying and firing have shown that warpage is reduced over 50%. In some clay wares, shrinkage is very important and here again a great advantage is gained. In a series of tests on bars, the shrinkage in the evacuated clay was absolutely uniform and somewhat less than in the unevacuated body.

The process is in daily use and has become standard practice. So greatly has the strength of the body been increased that those handling it for the first time made two or three grabs before they could detach a handful and then looked up in amazement asking what kind of clay it was.

It is interesting to know how large a block of clay can be successfully treated by the process and in what time. I am not in a position to give a definite answer to these questions, not having so far worked on masses larger than 12 inches through, but such pieces can be handled in 15 minutes successfully.

Many criticisms have been made of the process because of a failure to realize the magnitude of the forces brought to bear. If we have a 12-inch cube of clay in a cylinder evacuated to about 97% vacuum, we have a vacuum of 28.8 inches with the barometer at 29.7. Into such a chamber air would rush with a velocity of about 900 feet per second until the internal pressure had risen to 58% of the atmosphere; 900 feet per second is equal to more than 613 miles an hour and we have a mass of over 14 pounds per square inch impacting at this velocity. It may readily be seen that the compacting force is very large indeed. It is vitally necessary that the air inlet valves should be large and opened with great suddenness.

A mass of very plastic clay, by crutching in a lot of air, is enormously reduced in apparent plasticity and this is just what happens very commonly. If such an air-laden clay be subjected to a high vacuum, a considerable distention of the body takes place at first; next the greatly extended air vesicles begin to burst and the occluded air finds its way out of the body with increasing ease, as more and more bursting bubbles open a path toward the surface. The result of this is a cellular mass of clay, the cells of which are vacuous, but for the water vapor contained in them. At this high degree of vacuity the water is nearly at its boiling point and consequently gives off vapor very readily, thereby expelling a a larger portion of the previously contained air than would be possible if dry instead of moist evacuation were taking place. But since one volume of water will develop 1650 volumes of vapor at atmospheric pressure and furthermore since the volume of gas is inversely as the pressure, it will readily be seen how so small a loss of moisture, less than one-half per cent, can, under conditions of vacuity, expel practically all the contained air.

If this cellular mass is suddenly exposed to the impacting force of the 14.7 pounds at atmosphere, delivered, as it is, at the rate of over 613 miles an hour on all sides, it will readily be seen that the compacting force is very large. It is abundant to collapse the empty vesicles and bring their opposite sides into physical contact.

That this really does take place, the following demonstration may be cited: In a block of graphite crucible body, 13 x 13 x 15 inches was made a hole of 2½-inch diameter, reaching to the center. The opening at the surface was well-kneaded together and a husky protective piece of the same body was well-kneaded over this. The block so prepared was then subjected to the treatment. On cutting the block open with a wire, we were not able to find even a slight line indicating where the hole had originally been.

Northwestern Terra Cotta Co.,
Chicago, Ill.

HYDROGEN-ION MEASUREMENTS ON CLAY SLIPS[1]

By D. W. Randolph and A. L. Donnenwirth

ABSTRACT

A simple electrometric apparatus is described for determining the hydrogen-ion concentration of clay slips. Some measurements are given to show the relation between hydrogen-ion concentration and the properties of a clay and water mixture.

The effects of acids and alkalis on the properties of clay and water mixtures have received a great deal of attention because of the important relations of these effects to the manufacture of almost every type of clay ware. The addition of small amounts of acid or alkali affects the viscosity of clay slips and the way in which they act in the casting mold, and influences the plasticity and the dry strength of the dry clay. A means of examining the mechanism by which these changes are brought about is of interest to the manufacturer because in the means employed may lie a method of control of processes or of raw materials.

The accepted theory is that the properties of a mixture of clay and water are largely affected by the presence of colloidal material, and the study of such systems has followed the progress of colloid chemistry. The amount of colloidal material present in a clay and its "quality" largely determines the nature of the clay, while the acidity or alkalinity of the water is an important variable.

Numerous and often contradictory results are reported in regard to the effects of acids and alkalis of different strengths on the physical properties of slips and clay pastes. Evidently the action depends on many factors, such as the original condition of the clay as regards acid or alkaline content, the concentration of the clay in the water, the time of aging of the mixture, the strength of the added electrolyte, etc.[2] It would seem that a method for following the changes in acidity of the water portion would give information of value.

It is not the purpose of this paper to propose a means of slip control based on acidity measurements, or to point out ways in which these measurements may be useful but rather to describe a simple apparatus and to give some of the data we have collected in our experience with it.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (White Wares Division.) Received May 24, 1926.

[2] Leonor Michaelis, General Principles of the Effects of Ions in Colloids, 2nd Colloid Symposium Monograph, 1925.

The *p*H Value

When an acid is placed in water it dissociates more or less completely into ions and the effect of acidity is due to an increase in the concentration of the hydrogen-ion. Pure water dissociates slightly into hydrogen- and hydroxyl-ions and the H- and OH-ions are equal in concentration. When an acid is added to pure water increased concentration of the H-ion results, while the addition of a base increases the OH-ion concentration. The actual concentrations are represented by some such figure as 10^{-14} and the inconvenience of dealing with such a number is avoided by calling this negative exponent "*p*H." Thus the *p*H of a solution having a hydrogen-ion concentration of $10^{-2}N$ is 2, while the *p*H of pure water is 7. For an exact and detailed explanation reference may be made to Clark's book on the determination of hydrogen-ions.[1] This means of expressing the acidity or alkalinity of a solution has been highly developed and is in universal use among chemists both as a tool for research and as a means of control of industrial processes. Baking, canning, water supply purification, and leather tanning are among the industries that are familiar with the term *p*H and use it in everyday control of operations.

Determination of *p*H Value

Two methods for determining the hydrogen-ion concentration or *p*H are in use. One depends on the change of color of a standard indicator when added to the solution under examination. The resulting color is compared to that of a standard series of colored solutions. A clear liquid sample without turbidity is required which necessitates the filtration of the liquid from the clay. The electrometric method determines the *p*H by measuring the voltage set up between two standard electrodes when they are dipped into the solution. With care the electrometric method will give good results in thick clay slips and does not require special preparation of the sample.

The electrometric apparatus consists of two electrodes, one of hydrogen and the other of calomel. The hydrogen electrode is formed by the use of a layer of platinum sponge which is kept saturated with hydrogen gas. The calomel reference cell depends on the potential due to the equilibrium between mercurous ions and a mercury surface. The contact between this reference cell and the liquid under examination is made by means of a standard solution of potassium chloride. For a discussion of the theory of these electrodes, as well as complete and helpful directions as to their use, Clark's book is again referred to, and only a description of the mechanical details of the apparatus will be given here.

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[1] W. M. Clark, The Determination of Hydrogen Ions.

Figure 1 is a sketch of the electrodes, as made by the Leeds & Northrup Company. Two hydrogen electrodes are used, either of which may be connected to the potentiometer by means of a two-way switch. This gives a rapid way of checking a reading. The center portion of each hydrogen electrode is removable for cleaning or replating and consists of a straight glass tube with a piece of platinum wire sealed through the end. Platinum black is plated on the exposed end of the wire by electrolysis in a dilute solution of platinic chloride, and just before use the electrode is placed in a dilute solution of sulphuric acid as the cathode and saturated with hydrogen gas. The platinum black coating adsorbs many times its weight of hydrogen and the result is a hydrogen electrode in contact with the sample. Continued use of this electrode in a clay slip renders the electrode inactive and when this occurs the center portion is removed and may be cleaned and replated in a few moments.

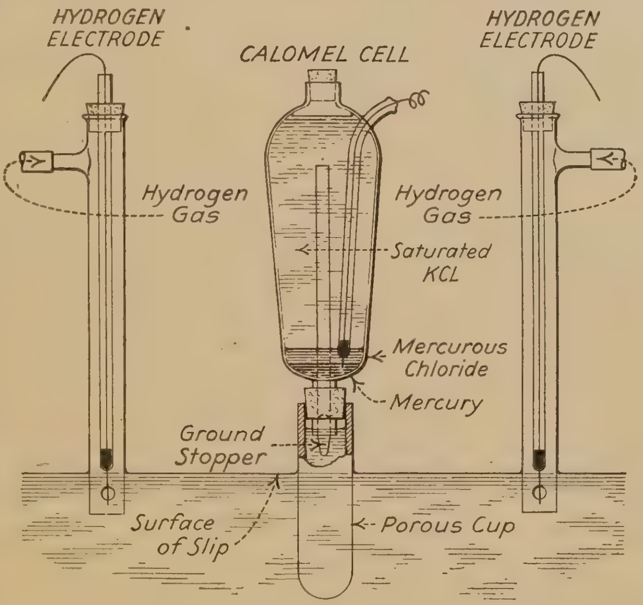

FIG. 1

The calomel cell is especially suited for use in clay slips because contact is made through a porous porcelain cup that prevents contamination of the cell by fine particles of clay. The cell is self-contained and there is no danger of dust entering. The KCL in the porous cup may be renewed easily if necessary, at which time the glass valve at the bottom of the cell prevents loss of solution from the cell itself.

All three electrodes are held in a support and may be inserted into a 400 cc. beaker which holds the sample under observation. A stirring paddle driven by a small motor is useful, and burettes may be mounted above the beaker for the addition of measured amounts of electrolytes. Hydrogen is supplied to the two hydrogen electrodes at a slow rate so that about one bubble of gas escapes from each electrode every second. We have used commercial tank hydrogen and have not found it necessary to purify the gas although this is very desirable. The measuring instrument must be of the potentiometer type as no current can be drawn from the electrodes without affecting their reading.

Hall[1] has examined the effect of changes in hydrogen-ion concentration on the flocculation and deflocculation of clays and has also determined the *p*H of slips formed by various clays in water. He shows the effect of the presence of clay in water when an electrolyte such as NaOH is added. The amount of electrolyte adsorbed by the clay is shown by the lower hydrogen-ion concentration as compared to that resulting from the addition of the same amount of electrolyte to water alone. Hall concludes that, in the case of the clay he used, the action was a physical one until a *p*H of 12 was reached after which a chemical action set in.

Report of Observations

In Fig. 2 are shown some data obtained with two ball clays, Kentucky and English. We have used a water-clay ratio of 12 to 1, while Hall used a ratio of 70 to 1, which accounts for the much larger apparent adsorption shown in our measurements. These curves were obtained after a measured amount of electrolyte was added, the slip thoroughly stirred and then allowed to stand for 24 hours. The electrolytes used were acetic acid and sodium carbonate.

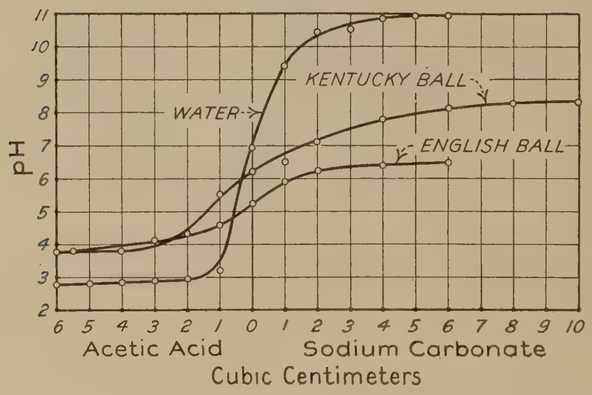

FIG. 2.—Adsorption of acids and alkalis by clays.

It is interesting to note that the adsorption of alkali is greater than the adsorption of acid, especially in the case of the Kentucky ball clay.[2] The initial *p*H of the slip is given by the intersection of the curve with the zero addition line. Evidently the English clay resists the action of the electrolyte that would tend to change the *p*H of the resulting solution more than the Kentucky clay. It should be noted that the difference is exaggerated by the fact that the English clay is more acid to start with than is the Kentucky clay.

The effect of the aging of a clay slip on its *p*H without the addition of electrolytes was investigated. Our results agree with those of Hall in that no change of any magnitude could be found in the case of Kentucky ball clay, English ball clay, Florida kaolin, or Delaware kaolin after aging for periods of from two to three weeks. Further work that is not completed indicates that the adsorption of the electrolyte by clay increases in some cases with the length of time the slip has aged; that is, the addition of an electrolyte to the aged slip does not cause as large a change in H-ion concentration as the addition of an equal amount to a freshly blunged sample.

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[1] P. Hall, *Jour. Amer. Ceram. Soc.*, 6[9], 989 (1923).

[2] Searle, The Chemical and Physical Properties of Clays and Other Ceramic Materials, p. 241.

These results apparently indicate that the amount and character of the colloidal or finely divided matter in a clay are both important in determining the action of the electrolyte. It may be possible that clay from the same source, but from different parts of the bed will vary greatly in reaction to electrolytes, due to the variation in amount and character of the colloidal portion of the clay.

In our plant water is supplied from the city mains and is subjected to various purifying and settling processes before we receive it. For a period of time we kept a record of the variations in the *p*H of the water from the mains and also of the viscosity of a slip made from Kentucky ball clay and this water, in the proportion of 50 grams of dry clay to 300 cc. of water. The results of this experiment are shown in Fig. 3 and indicate the close connection between the slight changes in acidity of the water and the viscosity of the ball clay slip. These data are interesting because they show the source of a variation in slip viscosity that would call for more or less electrolyte to correct it. It also serves to emphasize the fact that the hydrogen-ion measurements are directly related to some of the properties of the slip.

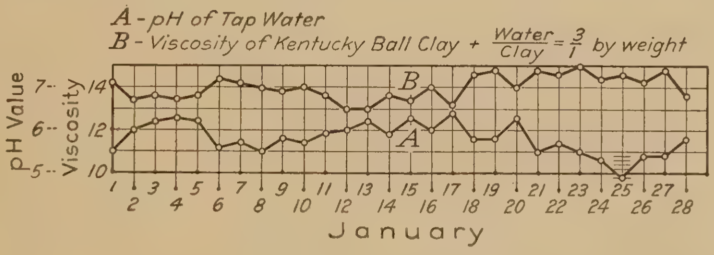

FIG. 3.

Schurecht[1] and others have called attention to the fact that the addition of electrolytes has an effect on the strength of clay pieces in the dry state. Schurecht mentions the use of sodium silicate, sodium carbonate, and calcium hydroxide in adding strength to a dry clay piece. In order to investigate this point we made up a series of batches of a spark plug body. The *p*H of successive batches was adjusted while the clay was in slip form in the ball mill. A number of bars were made up from each batch, dried under standard conditions and the breaking strength of these bars was determined. Figure 4 ows the relation between the breaking strength and the *p*H of the slip. The addition of sodium carbonate in most cases would weaken this body in the dry state, since it naturally tends to lie somewhat on the alkaline side of *p*H 7. No difference could be detected in dry strength when an adjustment to a given *p*H was made by means of different electrolytes. One of the points at the maximum of the curve represents a body adjusted by means of acetic acid, another by the use of hydrochloric acid, and the third by the addition of sodium silicate to a batch that was first made acid by mistake. This tends to show that there is a definite relation between dry strength and the H-ion concentration of the water phase of the system. While in many cases the dry strength of a body is ample, still one explanation of periodic weakness and resultant loss in handling may lie in slight changes in the acidity of the slip, due either to differences in the clays used or to changes in the water supply.

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[1] H. G. Schurecht, *Jour. Amer. Ceram. Soc.*, **1,** 201 (1918).

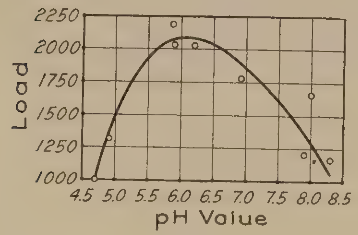

FIG. 4—Effect of *p*H on dry strength of spark plug body.

In the casting of clays the effect of slight changes in acidity or alkalinity are important; and changes in H-ion concentration rather than additions of a particular electrolyte by volume may explain some of the puzzling things that occur. For instance, a change in one of the clays used may make necessary the use of more or less than the usual amount of electrolyte for a time. Figure 5 shows the relation between the viscosity of a Kentucky ball clay and the *p*H of the water, through the range generally used in casting. Over a very short range the viscosity was the same at a given *p*H regardless of whether the electrolyte was sodium carbonate or sodium hydroxide on the basic side, or whether acetic acid or hydrochloric acid was used on the acid side. In the range of alkalinity beyond a *p*H of 10, however, this was not true; sodium hydroxide, for instance, producing a thicker slip than sodium carbonate. This is probably due to chemical action of some kind between the organic salts originally in the clay or to chemical action on portions of the clay itself. The English ball clay used in our experiments showed much less change in viscosity with changes in *p*H and the results in some cases were so erratic that we have not included this curve as there was no time to thoroughly check the results. Apparently, in the case of No. 25 English ball clay, there was a chemical action of some kind which took place at a *p*H of 4.3 that caused a decrease in viscosity

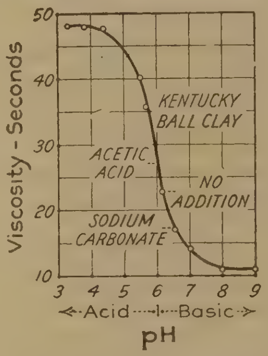

FIG. 5.—Viscosity-H-ion concentration. Water/clay = 2/1.

instead of the expected increase. The action on the basic side as far as a *p*H of 10 was normal. There is evidence that chemical action of some kind occurs in the case of all alkaline hydroxides at even very low concentrations. The relation between *p*H and viscosity is not a definite one for any particular clay and depends largely on the electrolyte used.

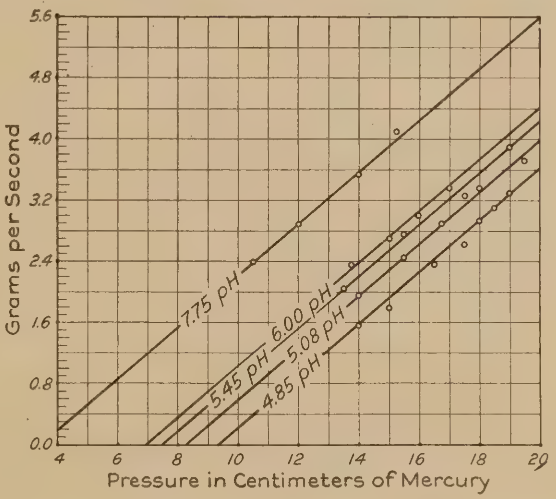

Fig. 6.—Kentucky ball clay–old mine No. 4. Bingham Plasticity Curve.

The effect of a change in *p*H on the plasticity of Kentucky ball clay as measured by Bingham's method is shown in Fig. 6. Bingham considers plasticity as dependent on two factors—mobility and yield point. Changing the *p*H of this ball clay does not change the slope of these curves, but the "yield value" or point of intersection with the axis of the curves changes in proportion to the *p*H value. This seems to hold for several clays, but it is probable that there is no very definite relation between *p*H and yield value when different electrolytes are used with the same clay.[1]

The measurement of hydrogen-ion concentration should be of value to anyone dealing with clay products made by either the plastic or casting process. It cannot be substituted for other means of control, but may prove extremely useful and an important help in dealing with clays in slip and plastic forms.

A. C. Spark Plug Company
Flint, Michigan

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[1] E. C. Bingham, Fluidity and Plasticity, p. 232.

FIRING TERRA COTTA IN AN OPEN KILN[1]

By O. E. Mathiasen

ABSTRACT

Tests on firing terra cotta in an open oil fired kiln are described. A full description is given of the special flue and combustion chamber design used in the kilns. Results of the tests were entirely satisfactory and justify further experiments along this line.

Very few known attempts have been made to try the practical possibilities of firing terra cotta, or for that matter any glazed ware, without a muffle or in an open kiln. In most tests the fuel used was gas, not coal or fuel oil. There has been quite some talk about firing terra cotta in an open kiln, but as far as we know, this is the first attempt on anything like a practical basis, using oil as a fuel.

Three separate firings were made. The first in a kiln at the General Ceramics Company, at their Keasbey plant through the courtesy of F. A. Whitaker, and the last two at the plant of the Carborundum Company, through the courtesy of E. B. Forse. The kilns in both cases were regular rectangular kilns with special flue and combustion chamber construction as designed by the Carborundum Company. B. M. Johnson of the latter Company delivered a paper before the New Jersey Clay Workers Association in which he described this special combustion chamber as follows:

> The carboradiant combustion chamber in the form particularly adapted to kiln firing consists of two rectangular flues, one superimposed on the other, built up of relatively thin silicon-carbide tile as illustrated in Fig. 1. The extension of the lower section is built into the kiln wall and into this opening the oil is fired. The lower flue connects with the upper at the end away from the burner and the gases thus return toward the burner. The tile forming the top of the upper flue are spaced to permit egress of the gases along the entire length. These combustion chambers are placed on either side of the kiln space as illustrated in Fig. 1 and, depending on the length of the kiln, either two or four chambers are used requiring either two or four burners. Between the chambers and the ware being fired stands a thin permanent bag wall that serves three purposes: (1) to permit the combustion chambers to run hotter than the ware particularly during early firing, (2) to direct the gases of combustion to the top of the kiln, and (3) to offer a means of regulating the application of heat to the ware by variations in its construction.
>
> The operation of these chambers is very simple. A small quantity of oil is discharged into the entrance, and the lower flue heats up rapidly so that good combustion is attained within a very few minutes. Then the proportion of excess air is reduced so that combustion takes place throughout the entire length of the lower flue. The upper flue rapidly reaches the temperature of the lower flue by contact with the hot gases and by transmission of heat through the thin tile forming the partition between the two. From this time the entire chamber is uniform in temperature from end to end because as the general temperature of the chambers is raised the radiation through the partition

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Terra Cotta Division.) Recd. May 7, 1926.

tile compensates for the gradual loss in temperature of the gases during their travel through the two flues.

Control of the fire is maintained by observation through small peep holes in the wall of the kiln above the burners. Sufficient air is admitted with the oil to complete combustion within the chambers and observation of the exhaust ports on the top of the chambers indicates this condition.

Using this means of combustion offers a number of advantages in heat application and kiln operation, both equally important in ceramic processes. The chambers furnish a radiant heating element of uniform temperature from end to end of the kiln instead of a series of hot and cold spots from a number of fireboxes. By proper outlet spacing they distribute the gases of combustion uniformly along its length. In the construction of the bag wall even temperature from top to bottom of the kiln may be obtained, as the construction readily permits a number of variations through its walls in heat flow although for ordinary kiln heights the increased radiation through its lower portion compensates for the loss in sensible heat of the gases in their downward flow through the ware.

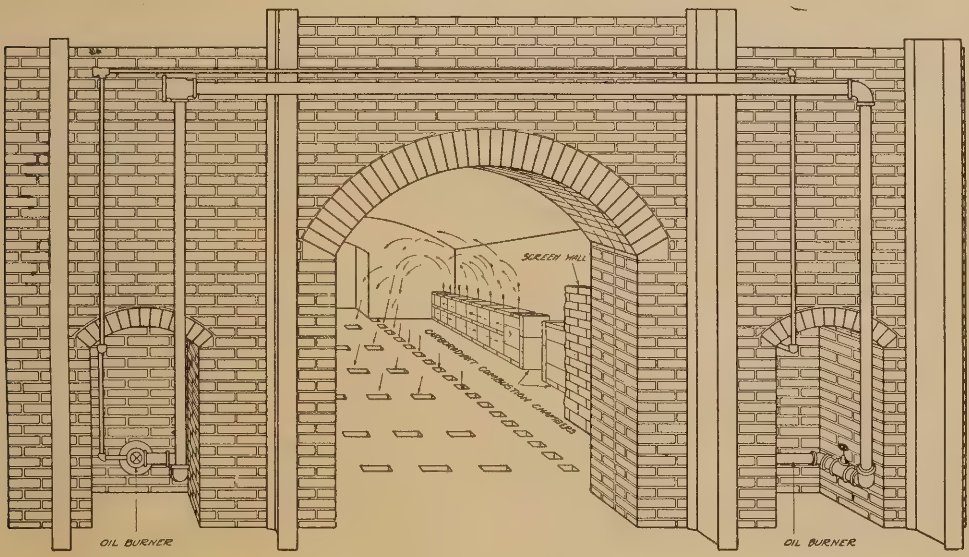

FIG. 1.—Carboradiant kiln—showing arrangement of chambers.

These chambers offer a simple means of visual control from a few burners, particularly for ware demanding regulation of atmosphere. Combustion can be maintained with either oxidizing or reducing conditions without sacrifice in efficiency. If flame is discharging from the outlet ports reducing conditions result, and if combustion is complete within the chamber the atmosphere is oxidizing. These conditions can be maintained without a great excess of air or dense volumes of smoke.

As a combustion device for oil the conditions furnished are ideal, as a temperature sufficient to support combustion is quickly reached. The small cross-section area of the flues gives an intimate mixing of oil and air. The long gas travel in contact with surface hot enough to support combustion permits the reduction of excess air to a minimum.

The rate of firing was typical of a small kiln, a slow increase for 10 hours then a straight line to complete the burn after about 60 hours firing to cone 5 down. CO_2 readings varied from 12 to 14% during the run from about 10 hours to end.

The ware in kilns was typical of a terra cotta plant. Pieces of terra cotta of all shapes and sizes, colors of all polychrome shades, and all of our regular finishes, matt and full glazes, unglazed plain and speckled, spattered finishes, glazed and unglazed, all on both regular pieces and samples.

The first firing was very satisfactory; all colors were exact duplicate of results in a true muffle kiln.

On the second firing, through error in instructions, the operator overfired the kiln with the result that all glazes, etc. were overfired. We did not take any stock in the results of this firing as the final temperature reached was much higher than that usual for terra cotta.

The third and final firing was entirely satisfactory. All colors and finishes were their regular shades. There was one color, however, which did not duplicate itself in any of the firings. This is a spattered and spotted unglazed texture color with a ground coat containing a small percentage of red clay to give a pink tone. In the open fire, this pink tone was not nearly as pronounced as in a muffle kiln. A change in slip ingredients would probably remedy this.

Polychrome colors were satisfactorily uniform.

These tests were carried out solely to prove the possibilities of firing terra cotta in an open kiln. On account of the small size of the kiln little attention was given to oil consumption although it ran around 95 gallons per fired ton of terra cotta.

The results of these tests justify further experimenting in designing and adjusting kilns for firing terra cotta and other glazed wares in an open kiln with oil as the fuel.

New Jersey Terra Cotta Co.
Perth Amboy, N. J.

A NEW TYPE OF DRIER HEATER[1]

By Charles F. Geiger

ABSTRACT

A novel design of a combination air heater and combustion chamber burning liquid or gaseous fuel is presented and illustrated with a drawing. Desirable features of independent drier heaters are outlined, and the efficacy of the equipment described in approaching the ideal achievements is demonstrated. Mention is made of the application of this type of heater to a number of different processes as well as to the heating of factory buildings.

Introduction

In many plants an independent drier heater is either a necessary or desirable means of supplying heat for drying processes. An ideal self-contained heater to be satisfactory must, fundamentally, be economical of fuel and labor, and it must afford continuous service with minimum supervision and maintenance. The successful heating unit, moreover, essentially produces clean gases so as not to injure the ware or inject obnoxious fumes into the working buildings. It needs, also, possess simplicity of operation and construction as outstanding features and be sufficiently flexible to permit of considerable variation in the output of heated air supply.

It is believed that the drier heater to be described embodies to a high degree practically all the advantages of the ideal drier heater. Before passing to a description, however, it might be well to detail briefly some of the disadvantages of the particular system that the new heater was designed to supplant.

A single, coal-fired pit-furnace was formerly employed for each group of three double-track tunnel driers each of 114 feet length. An exhauster fan situated above the loading end of each three driers supplied the draft for the fireboxes and induced the flow of hot gases, air, and evaporated water through the driers to the stack leading through the overhead roof. This equipment though functioning entirely satisfactorily for drying purposes was inherently insufficient in several respects all of which either directly or indirectly exerted an influence on the cost of operation. Coal had to be hauled to the fireboxes and ashes removed. Drier firemen were necessary twenty-four hours a day throughout the year. A considerable quantity of soot was deposited upon the ware and in the drier tunnels; this had to be brushed from the ware to allow of subsequent treatment previous to setting. The driers—roofs, sides, and floors—had to be thoroughly cleaned every three or four months. The atmosphere within the driers, due to the imperfect combustion in the fireboxes, was at least unpleasant for drier

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[1] Received April 7, 1926.

operators who frequently had to work within the tunnels as the congested situation of the driers did not permit of mechanical means of car propulsion. Another and one of the worst objections to the system was the fire hazard. Sparks from the fireboxes caused ignition of the wooden pallets and the greasy soot. These fires aided by the exhaust fan frequently gained tremendous headway before being discovered and caused heavy losses of ware and pallets, and even seriously damaged the motors driving the exhausters because the entire flue system, being soot laden, afforded ready propagation for flame travel all the way to and through the fans. Even though a fire were discovered in a relatively early development, damage caused by fire and water to twenty-eight large drier cars loaded with silicon-carbide refractories could readily run into several thousand dollars. Then again three or four fires of this nature meant increased insurance rates for the entire plant. It is easy to comprehend, therefore, that the system though entirely adequate as far as mere drying was concerned was insufficient when all costs and inconveniences were considered.

Description of Carboradiant Direct-Fired Drier

The drier heater installed consists of the very simple structure illustrated in the drawing. The shell, which is insulated, is built of fire brick; this surrounds the 8-foot combustion chamber which is made up of thin special-shaped, interlocking silicon-carbide tile to form a rectangular flue running parallel to the length of the shell. The burner feeds in through the front wall and combustion takes place throughout the length of the carborundum chamber; the supply of primary and secondary air is adjusted so that combustion is entirely complete within the silicon-carbide flue so that no flame can be seen issuing from the two outlets. As it becomes necessary to increase the rate of burning the oil, more air is supplied through or around the burner so that all combustion is still maintained within the chamber. The long travel of the gases within relatively narrow confinement necessitates complete mixture of oil-vapor and air. Because of the incandescence of the walls throughout the length of the carborundum chamber and the absolute control of the primary and the secondary air it is always possible to effect complete combustion within the firing flue so that no unburned gases are discharged from it.

The air to be heated is induced into the shell through the adjustable louvers in the front wall. The baffles compel the air to pass across the furnace providing a good wiping action against the incandescent chamber thereby affording an efficient heat transfer. The inner fireclay walls and crown of the shell are built with projections in alternate rows of brick; the latter are heated by radiation from the furnace and likewise transmit heat to the air passing their surfaces. The heated air receives a further temperature increase on being mixed with the products of combustion issuing from the chamber just previous to the passage that leads to the header flue in front of the drying tunnels.

The louver in the flue beyond the heater is of use at those times when only a very small quantity of heated air may be desired or when the final air temperature is to be very low. In either circumstance the front wall louvers are closed, and the products of combustion are tempered as required with air entering the rear louver. It is preferable on very low air requirements to operate in this manner in order that the carborundum furnace may be maintained at a red heat so that complete combustion is facilitated. When a drier of this type is used for supplying hot air for spray drying food products or chemicals the gas outlet shown in the drawing is employed only for a very few minutes in starting up and during this time the damper in the flue leading to the drier is closed.

The oil from the main storage tank is distributed by a small gear pump requiring one-horse power. A low-pressure air-atomizing burner employing six ounce primary air has its air supply furnished by a small fan requiring three-horse power at maximum blower capacity of 600 cubic feet per minute which is about 300% over the amount required for normal operation of this particular unit. The secondary air is induced around the burner. The motor sizes are given to show the small amount of electric energy necessary to operate the equipment. The total cost of the electric power required by both motors is from 3 to 7½ cents per hour.

Costs and Savings

A drier heater of this type costs two thousand to twenty-five hundred dollars completely installed, including all mechanical and electrical equipment, materials, labor, and erection costs. This heater operates on an oil consumption of 1.3 to 2.5 gallons per hour per drier depending upon the temperature desired. An average of 108 gallons of oil per day for three driers promotes faster drying than the ton of coal required per twenty-four hours with the old system. These figures demonstrate the efficiency of the oil-burning equipment, which also has none of the disadvantages formerly encountered. There is no soot whatever, and consequently the ware and the driers do not require cleaning. There is no smoke at any time, and, of course, coal and ash haulage are cost factors no longer. The important saving in operation, however, is the elimination of drier firemen. The system requires attention once every three or four hours only and this little work has been transferred to the tunnel kiln firemen. This saving is $12 per twenty-four hours or over $4000 per year so that the installation paid for itself in labor saving alone in approximately six months.

This heater has been operated for over two years and there have been no drier fires during that period. There is no firebox to burn out and only three or four tile have had to be replaced from breakage in 17,000 hours of practically continuous operation. Repairs to the shell are not anticipated as there is no flame impingement on the fire brick, which, incidently, barely reach a red heat.

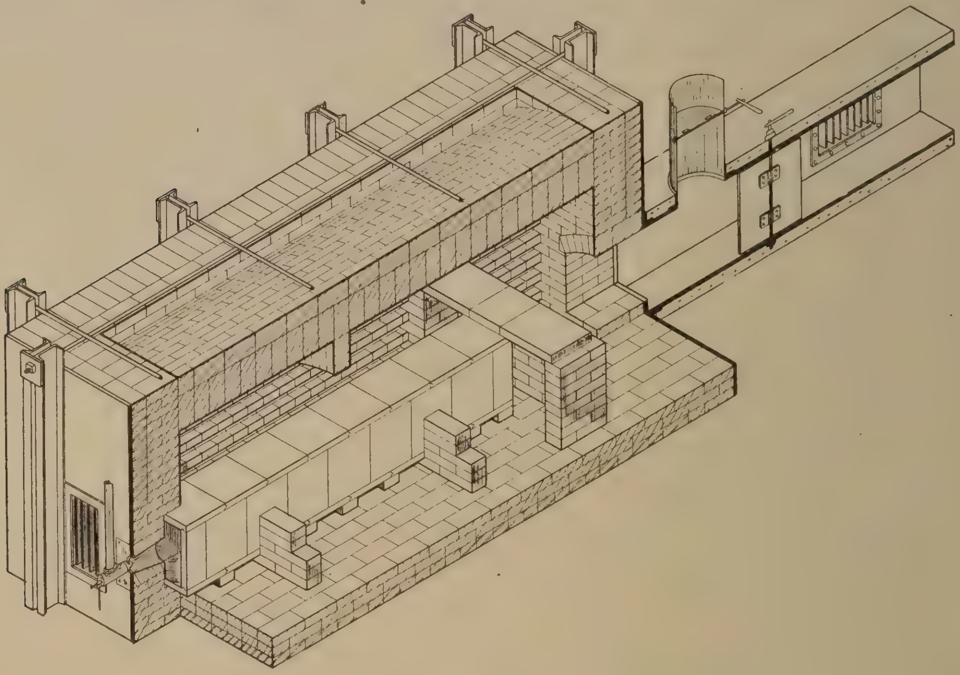

FIG. 1.—Carboradiant air heater—direct fired.

There seemingly is no reason why humidity drying with gas recirculation could not be coupled in many cases with this heating unit which obviously is more efficient in heat transfer than indirect steam heating.

The efficacy of the combustion chamber in producing complete combustion is demonstrated by the fact of the successful application of this method of heating air that is admixed with the products of combustion to the spray drying of such food stuffs and chemicals as baking soda, salt, Glauber's salts, and chrome tanning compound. This type of combustion chamber and air heater is being applied also to rotary driers. One of these heaters is being designed, also, for a combination of drying ceramic ware and heating factory buildings. In this case part of the heated air will be removed from the furnace previous to its admixture with the products of combustion. This is to be conveyed through ducts and discharged at sundry points for supplying heat to the building. The burned gases are to be mixed with air and this product will be used for the drying of sanitary ware.

THE CARBORUNDUM COMPANY
REFRACTORY DIVISION
PERTH AMBOY, N. J.

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PROGRESS REPORT ON INVESTIGATION OF SAGGER CLAYS—SOME OBSERVATIONS AS TO THE SIGNIFICANCE OF THEIR THERMAL EXPANSIONS.—II[1]

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ABSTRACT

This is the second Progress Report based on data obtained in an extensive investigation of sagger clays, conducted for the purpose of determining the properties characterizing clays best suited to this type of service. The report contains a brief description of the apparatus used in the determination of thermal expansion from room temperature to 1000°C together with a correlation of the thermal expansions determined with the physical properties of the clays as given in the first Progress Report. For the clays examined the information obtained indicates that: (*a*) there are two types of clays as characterized by thermal expansion, between 100 and 200°C, and resistance to failure when subjected to sudden temperature changes similar to those encountered in service; (*b*) repeated firings tend to develop increased expansion between 100 and 200°C and, consequently, decreased resistance to failure when subjected to sudden temperature changes; and (*c*) that additions of corundum to clay tend to increase the average, but decrease irregular, thermal expansions.

I. Introduction

In the first Progress Report of this investigation[2] data are given which served as a basis for the grouping or classifying of the fifty-one clays according to their firing characteristics. As stated in the Report, it was proposed to continue the work by a more fundamental study of the clays. Accordingly an apparatus was developed to determine rapidly and with satisfactory accuracy the thermal expansion of specimens sufficiently large to represent adequately commercial bodies. The expansion of forty-nine clays, as well as of several mixtures of clays and of clay and corundum, were observed from room temperature to 1000°C.[1]

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[1] Published by permission of the Director of the U. S. Bureau of Standards, Department of Commerce. Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Atlanta, Ga., Feb., 1926. (White Wares Division.)

[2] *Jour. Amer. Ceram. Soc.*, 9[3], 131–43 (1926).

This paper reports the results of the determinations together with some observations of the expansion characteristics and of the apparent relation of thermal expansion to porosity and resistance to failure in an air-quenching test. For a few clays the effect of repeated firings, and of additions of corundum on thermal expansion was also studied.

II. Description of Specimens

Specimen bars which had previously been fired at 1230°, and broken in determining modulus of rupture, were cemented together, dried at 110°, and a "seating" drilled in each end. The seating was approximately $\frac{5}{8}$ inch deep and of sufficient diameter to form a "loose fit" with the fused quartz rods (Fig. 1) which supported the specimens in the furnace and transmitted the expansion to the gages.

The specimens were about one inch square in cross-section and seven inches long. The distance between the bottoms of the seatings, averaging 5$\frac{3}{4}$ inches, was measured to one-thousandth of an inch for each specimen on an end standard comparator, using an Ames gage as an indicator, since it was for this distance (or length of specimen) that the expansions were determined.

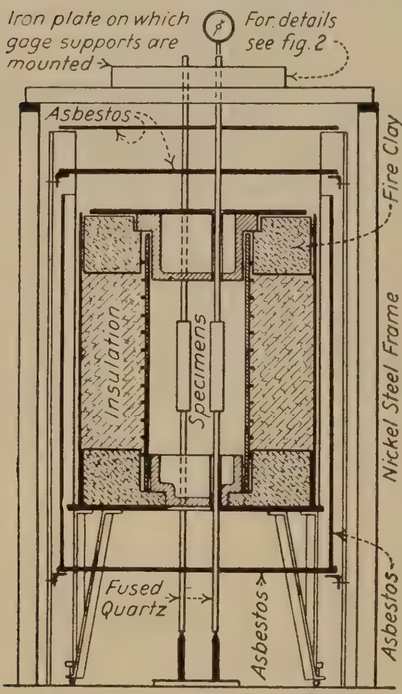

FIG. 1.—Assembly sketch of furnace and apparatus used in the determination of thermal expansions.

The bars were made of 50% clay and 50% grog. The grog in each case was of the same clay as the bond and had been calcined at 1200°C. For the chemical compositions of all the clays, and for the previous thermal history of those clays and bodies used in studying the effect of repeated firings see the first Progress Report.[2]

Since the specimens broke with a clean fracture, in the test for modulus of rupture, the error introduced by the very thin layer of cementing material (sodium silicate) was not considered measurable. The particular specimens previously fired at 1230° were used because the trial saggers used in the quenching test had been fired at this temperature (which is intermediate between the maximum temperatures attained in industrial kilns for semi-vitreous and vitreous ware).

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[1] In this Report all temperatures are expressed in degrees C.

[2] *Loc. cit.*, pp. 134 and 141.

III. Description of Apparatus

The construction of the apparatus used in determining expansion coefficients is indicated by the sketch in Fig. 1. It is relatively crude and was not designed for precision measurements.

The furnace proper is of the vertical muffle electrically heated type, the heat being generated in chromel wire coils placed in the upper and lower ends and as a spiral against the outside surface of the muffle. The current to the coils in the ends, and the three units comprising the spiral, can be controlled independently enabling the operator to maintain a satisfactory temperature uniformity.

Three specimens can be observed simultaneously. Each specimen is supported by a fused quartz rod and the expansion is transmitted to a gage (Fig. 1) by another rod of the same material. Asbestos shields, to localize heat radiated from the furnace, are supported on an iron frame not in contact with the furnace and the gages are supported by a third frame, made of nickel-steel. In this way the test specimen and the fused quartz rods, the furnace, the asbestos shields and frame, and the frame supporting the gages can expand and contract independently.

Expansions (or contractions) of $\frac{1}{20,000}$ inch can be read on the gage dials, which were calibrated in the Bureau to this accuracy. A movement of $\frac{16}{10,000}$ inch at the end of the gage lever (Fig. 2) causes the needle to make one revolution of the dial. Since the expansion to be measured usually exceeds $\frac{16}{10,000}$ it was necessary to so mount the gage that it could be raised or lowered, as required, to bring the needle back to zero. The three gages and the method of mounting are shown in Fig. 2.

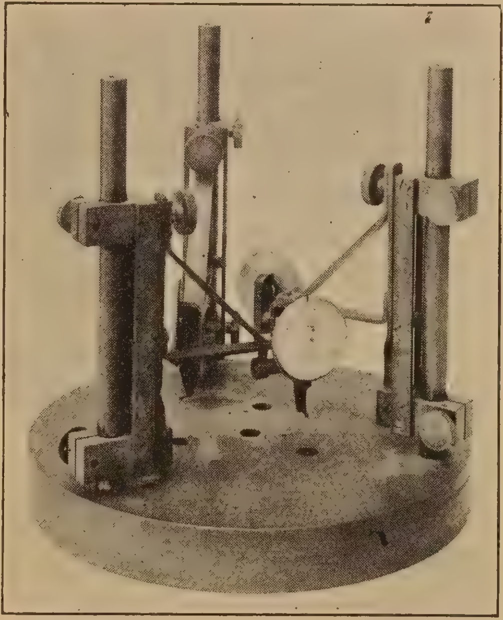

FIG. 2.—Showing method of mounting the gages which were used in measuring thermal expansion.

The set-up of the apparatus and specimens is accomplished by placing the test specimens on the lower fused quartz supports while the top of the muffle, upper asbestos shields, and gage support are removed. The top of the muffle is then replaced and the upper fused quartz rods inserted through the muffle top and into the seatings in the specimens, after which the asbestos shields which protect the gage support and gages from the heat of the furnace can be laid back on the iron frame. The gage support is then placed on the outer nickel-steel frame and the gages adjusted.

The thermocouples necessary to properly control the temperature within the muffle are admitted through the bottom of the furnace and are semi-permanently installed.

From eight and one-half to nine hours are required to complete a test. In this investigation the temperature was raised quite rapidly through approximately 100-degree intervals and held for about 5 minutes after no further expansion was noted (for typical schedule see Fig. 5).

IV. Calibration

The expansions recorded by the gages (Figs. 1 and 2) are not the direct expansions of the test specimens but the total expansions of the specimens, the fused quartz rods, and the supports for the gages. The correction curve (or constant) for the apparatus was determined by observing the total expansion using three fused quartz specimens whose true expansion was known[1] (from room temperature to 1000°) and calculating the difference between the observed expansion and the known true expansion of the specimens alone. Since the curve applies to this particular apparatus only, it is not shown but it may be stated that the correction averaged approximately 10% of the thermal expansion of the specimens as determined in this work.

The calibrated apparatus was used in testing materials whose thermal expansions varied from that of fused quartz to that of fused alumina, and in a laboratory in which the temperature varied from about 18° at the beginning of the test to 26° at the end of the test. No data have been obtained to show the probable accuracy for materials of greater or lesser expansion than those tested, or when made under other conditions of room temperature.

V. Precision

1. Observations on Heating

The accuracy of the calibrated apparatus was determined by measuring the expansion of specimens of porcelain and zirconium silicate and comparing the results with results obtained in the Thermal Expansivity and Interferometry Sections of the Bureau.[2] It was found that the maximum average variation in coefficient of expansion for a two-hundred degree temperature range was 0.2 x 10^{-6} per degree C, which is equivalent to an accuracy of approximately ±2.5%. The data are summarized in Table I and shown in Figs. 3 and 4.

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[1] See forthcoming Bur. of Stand., *Sci. Paper*, No. 524, "Measurements of the Thermal Expansion of Fused Silica."

[2] The method used in the Thermal Expansivity Section will be described in the forthcoming Scientific Paper referred to in above footnote . The method used in the Interferometry Section is described by Peters (*Jour. Wash. Acad. Sci.*, 9[10], 281 (1919)) and Merritt (Bur. of Stand., *Sci. Paper*, No. 485). See also G. E. Merritt and C. G. Peters, "Interferometer Measurements of the Thermal Dilatation of Glazed Ware," *Jour. Amer. Ceram. Soc.*, 9[6], 327–42 (1926).

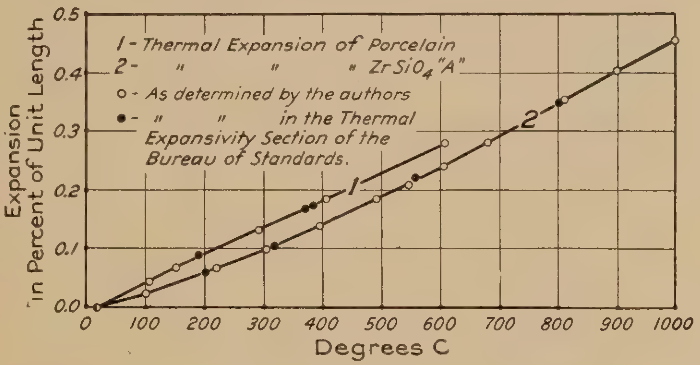

FIG. 3.—Curves showing agreement of results obtained in this investigation with results obtained in the Thermal Expansivity Section of the Bureau of Standards on the same material.

The temperature uniformity within that area of the furnace occupied by the specimens was observed by means of nine base metal thermocouples, one couple being placed at the bottom, one at the top, and one midway of each specimen. The temperatures were recorded to the nearest ¼ millivolt (equivalent to the nearest 6°) and the current to the heating coils was so controlled that the temperature gradient, as observed by the nine couples, did not exceed 12°. The temperature record of a typical test is given in Table II and the maximum and minimum temperatures for this test are shown by the two curves in Fig. 5.

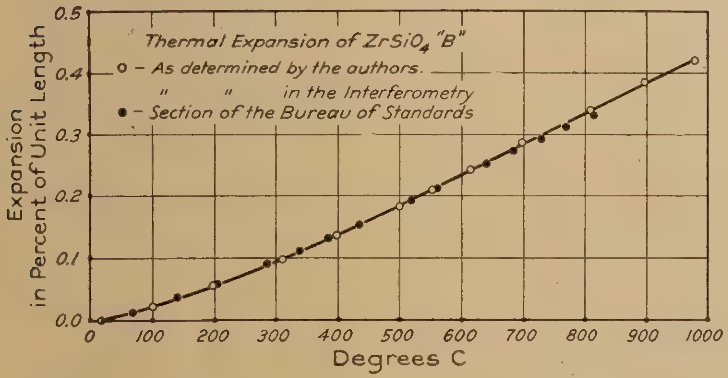

FIG. 4.—Curves showing agreement of results obtained in this investigation with those obtained in the Interferometry Section of the Bureau of Standards on the same material.

2. Observations on Cooling

It was found to be impossible to control the temperature during cooling within the area occupied by the specimens to closer than 30°. Consequently, the accuracy of observations on cooling is less than on heating. Under these conditions the plotted values obtained on cooling zircon and fused quartz practically followed the expansion curves on heating but dropped below those for the clays in the range from 600 to 300°. This showed an appreciable change in rate of expansion due to the $\alpha \leftrightarrows \beta$ quartz inversion.

Observations were taken following a number of the tests, and after the apparatus had reached equilibrium at room temperature, to determine whether or not the gages would come back to zero. With the exception of clay Number 39, which showed a slight permanent contraction (about 0.1%), the gages came back to within $\frac{5}{10{,}000}$ of zero. This indicates a negligible permanent expansion (or contraction) in the length of the specimens and also demonstrates that the sodium silicate used to cement the pieces produced no noteworthy permanent change during the tests.

VI. Results

The data obtained with individual clays fired at 1230°C are given in Tables III and IV. Typical curves are shown in Figs. 6, 7, and 8. As is evident, the curves have been grouped according to the thermal expansion behavior from 100 to 200°; clays of Group L (Table III and Figs. 6 and 7) showed a decided increase in the rate of expansion while clays of Group H (Table IV and Fig. 8) showed a very small or, in the majority of cases, no increase in rate of expansion.

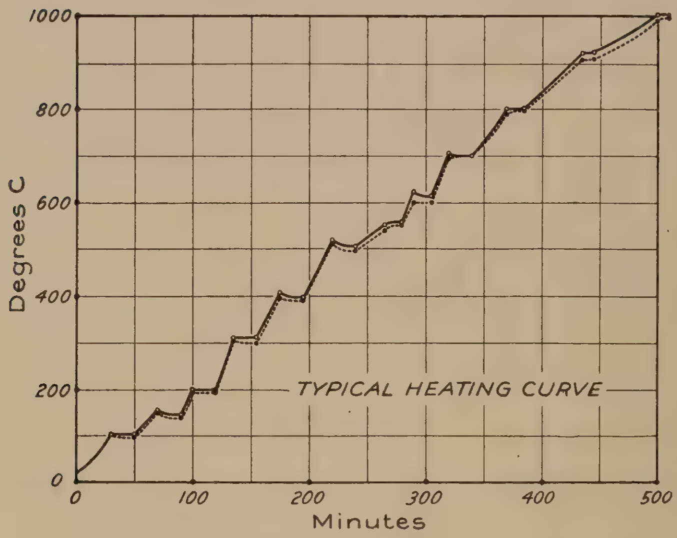

Fig. 5.—During each test temperature readings were taken at top, midway, and bottom of each of the three specimens. The two curves in this figure show the maximum and minimum temperatures recorded by the nine thermocouples during a typical test.

Table I.

(1) Observations obtained with apparatus described in this paper
(2) Observations obtained in Thermal Expansivity Section
(3) Observations obtained in Interferometry Section

Average Coefficient of Expansion $\times 10^{-6}$

Temp. Range	Room temp. to 200°		200°–400°		400°–600°		600°–800°		Room temp. to 800°	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Porcelain	5.2	5.2	4.2	4.4	5.1	4.9	—	—	—	—
Zircon "A"[a]	3.4	3.3	4.1	4.1	5.0	5.1	5.2	5.1	4.4	4.4
	(1)	(3)	(1)	(3)	(1)	(3)	(1)	(3)	(1)	(3)
Zircon "B"[b]	3.2	3.2	4.1	4.1	4.9	4.9	5.0	5.2	4.3	4.2

[a] Zircon "A" (Fired to 1450°C)—$\begin{cases} \frac{2}{3} - \text{100-mesh zircon} \\ \frac{1}{3} - \text{200-mesh zircon} \end{cases}$

[b] Zircon "B" (Fired to 1485°C)—Zircon "A" bars crushed and ground to pass an 80-mesh sieve.

TABLE II

Temperature Readings Taken during a Typical Run and Showing Temperatures at Top, Midway, and Bottom of Each of the Three Specimens.

Time in minutes	Specimen A			Specimen B			Specimen C		
	Top °C	Mid °C	Bot °C	Top °C	Mid °C	Bot °C	Top °C	Mid °C	Bot °C
30	103	103	103	103	103	103	103	103	103
50	103	103	103	103	103	98	103	103	103
70	150	155	150	150	150	150	150	150	150
90	144	144	144	144	138	144	144	144	144
100	199	199	194	199	199	199	199	199	199
120	194	199	199	199	194	199	199	194	199
135	304	311	304	304	304	304	304	304	311
155	311	311	297	311	304	311	311	311	297
175	407	407	401	407	407	407	407	407	395
195	389	395	389	395	389	395	395	395	389
220	511	517	511	517	517	517	517	517	511
240	500	505	500	505	494	505	505	500	500
265	546	552	540	552	546	546	546	546	546
280	558	558	552	558	558	558	558	558	552
290	611	617	599	611	605	605	605	605	599
305	605	611	599	611	599	605	605	605	599
330	700	705	694	700	700	700	700	700	700
350	700	700	700	700	700	700	700	700	700
380	795	801	789	795	795	795	795	795	789
395	795	801	795	801	795	801	801	795	801
445	906	919	906	906	912	906	906	906	906
455	906	919	906	906	919	912	912	906	906
505	995	1001	989	995	995	995	995	989	995
515	995	1001	995	1001	995	995	995	995	995

1. Characteristics of Curves

(a) From Room Temperature to 100° For Group L the expansion in this temperature range varied from 0.04 to 0.08%, and for Group H from 0.02 to 0.06%. Although the inversions of tridymite ($\alpha\rightarrow\beta$, 117°C; $\beta_1\rightarrow\beta_2$ 163°C)[1] take place above 100°C, there appears to be a relation between expansions considerably below 100° and expansions from 100° to 200° for it is evident from the data that the expansions from room temperature to 100° are, generally, directly proportional to the expansions from 100° to 200°.

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[1] C. N. Fenner, *Amer. Jour. Sci.*, **36**, 331–84 (1913).

(b) From 100 to 200° The expansion for all clays of Group H was very nearly the same (approximately 0.06%) in this range (Fig. 8), but varied greatly with clays of Group L. In the latter group, clay No. 18 expanded 0.08% and clay No. 3 expanded 0.27%, while the majority varied between 0.10 and 0.16% and the average for the group is approximately 0.14%.

While there are no known inversions in this range (100°–200°) other than those of tridymite to account for observed changes in rate of expansion, microscopic examinations have failed to show the presence of tridymite.[1]

(c) From 200 to 300° The expansions observed in this range are again practically the same for all clays of Group H (No. 45 excepted)[2] and vary considerably for clays of Group L. Four clays of Group L (Nos. 3, 6, 20, and 23), and clay 45 of Group H, expanded more rapidly between 200 and 300° than between 300 and 500° indicating the presence of cristobalite. The other clays of Group H, which expanded uniformly (or practically so) from 100 to 500°, probably contained neither tridymite nor cristobalite; and the balance of the clays of Group L, which expanded practically uniformly from 200 to 500°, probably contained no cristobalite (see footnote, p. 570).

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[1] The following evidence for and against the presence of tridymite is offered for the reader's consideration (H. Insley, collaborator):

For 1. The inversions of tridymite are known to occur between 100 and 200° (Fenner *loc. cit.*).

2. There are no other known inversions in this range.
3. After repeated firings the expansion due to the $\alpha \rightleftarrows \beta$ quartz inversion is diminished (see Fig. 7) while the expansion between 100 and 200° is increased.

Against 1. Microscopic examination by two petrographers failed to show the presence of tridymite.

2. Braesco (*Annales de Physiques*, **14**, 5 (1920)) as well as Le Chatelier (La Silica, Revue, **1**, 20 (1913)) show curves which indicate that the expansion caused by the $\alpha \rightarrow \beta$ quartz inversion is 2 to 3 times as large as the expansions caused by tridymite inversions. In many of the curves shown in this report (Figs. 3, 4, and 5) the expansion between 100 and 200° exceeds that between 500 and 600°. The quantity of tridymite in these specimens must therefore be at least twice as great as the quantity of quartz. If this is true, it should certainly be observable microscopically; furthermore, such quantities of uncombined SiO_2 cannot be accounted for from the chemical compositions.
3. Appreciable cristobalite could certainly be expected in a body containing tridymite (except after very long heating or in the presence of certain fluxes) since it is always an intermediate product in the inversion of quartz to tridymite. Yet the expansion curves of only 5 clays (Nos. 3, 6, 20, 23, and 45) clearly indicate the presence of cristobalite. This fact suggests the further possibility that the inversion of cristobalite may be partly or wholly depressed below 200°C in clay bodies and, since it causes an expansion six or more times greater than the tridymite inversions, could easily account for the phenomenon observed.

[2] Clay 45 is unique in that it is the only clay investigated showing a markedly greater expansion from 200 to 300° than from 100 to 200°.

(d) From 300 to 500° No known inversions of SiO_2 occur in this range and it is noteworthy that the rate of expansion is nearly the same for all the clays tested. The total expansion varied from 0.100 to 0.140% and averaged approximately 0.115%. Expressed as the coefficient (per cent per degree C), this average value is 0.0000057 (which checks with results of previous investigators as summarized by A. B. Searle*). Since many clays of Group H expanded at approximately this rate (57×10^{-7}) from 100 to 1000°, and clays of Group L from 200 to 1000° this value is probably the average coefficient of expansion of sagger clay when unaffected by inversions of uncombined SiO_2.

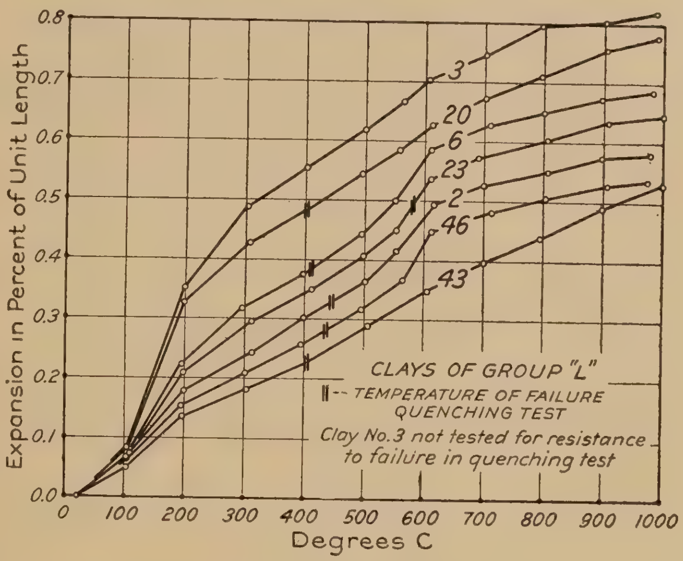

FIG. 6.—Thermal expansion curves of clays typical of Group L.

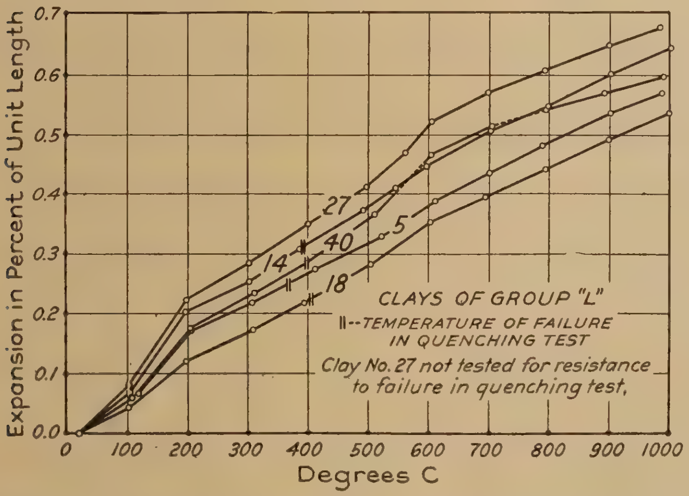

FIG. 7.—Thermal expansion curves of clays typical of Group L.

(e) From 500 to 600° The inversions of $\alpha \rightleftarrows \beta$ quartz[1] are probably the most generally known and discussed "expansion phenomena" in the ceramic industry. Approximately one half of the clays investigated showed a considerable increase in rate of expansion when heated

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* The Chemistry and Physics of Clays, pp. 570–573.

[1] F. J. Bates and S. M. Phelps, of the Polarimetry Section of the Bureau of Standards report the $\alpha \rightarrow \beta$ quartz inversion at 573.3°, and the $\beta \rightarrow \alpha$ quartz inversion as less sharply defined but probably between 572 and 573°.

TABLE III

DETAILED DATA GIVING THERMAL EXPANSIONS, AND TEMPERATURES AT WHICH OBSERVED, FOR CLAYS OF GROUP L

Clay No. A. Temperature at which expansion was determined, in °C
B Observed expansion, per unit length, at temperature indicated.

Clay No.												
1	A °C	108	199	310	408	511	—	610	698	789	896	1015
	B	.000536	.00146	.00205	.00246	.00349	—	.00449	.00482	.00510	.00555	.00587
2	A °C	103	199	312	399	501	553	615	699	808	897	978
	B	.000641	.00177	.00242	.00301	.00364	.00415	.00494	.00526	.00550	.00575	.00580
3	A °C	104	198	303	401	498	563	606	700	794	901	986
	B	.000823	.00351	.00488	.00555	.00619	.00667	.00705	.00746	.00796	.00803	.00817
4	A °C	103	198	303	403	492	551	600	708	794	915	1000
	B	.000648	.00225	.00287	.00344	.00390	.00431	.00478	.00534	.00568	.00614	.00633
5	A °C	120	207	307	412	523	—	612	702	790	903	989
	B	.000672	.00173	.00219	.00274	.00329	—	.00387	.00433	.00478	.00533	.00566
6	A °C	104	195	296	397	495	551	610	709	800	896	982
	B	.000667	.00222	.00319	.00375	.00443	.00500	.00586	.00628	.00650	.00673	.00687
7	A °C	119	200	304	407	511	—	608	701	794	894	1001
	B	.00074	.00215	.00273	.00330	.00391	—	.00486	.00543	.00555	.00587	.00626
8	A °C	103	198	303	403	492	551	600	708	794	915	1000
	B	.000576	.00198	.00246	.00318	.00370	.00406	.00433	.00481	.00538	.00590	.00623
9	A °C	103	198	303	403	492	551	600	708	794	915	1000
	B	.000656	.00182	.00229	.00274	.00321	.00353	.00381	.00456	.00498	.00554	.00594
10	A °C	102	194	305	392	481	554	612	699	801	896	993
	B	.000585	.00232	.00284	.00332	.00381	.00430	.00478	.00515	.00556	.00597	.00624
11	A °C	104	195	296	397	495	551	610	709	800	896	982
	B	.000737	.00186	.00228	.00280	.00335	.00375	.00408	.00463	.00510	.00549	.00582
12	A °C	105	197	303	387	493	547	598	704	800	904	1005
	B	.000619	.00195	.00239	.00284	.00339	.00371	.00402	.00459	.00505	.00562	.00605
13	A °C	105	197	303	387	493	547	598	704	800	904	1005
	B	.000625	.00218	.00282	.00327	.00390	.00447	.00479	.00525	.00558	.00603	.00629
14	A °C	105	197	303	387	493	547	598	704	800	904	1005
	B	.000696	.00203	.00253	.00307	.00371	.00408	.00444	.00502	.00543	.00597	.00641
16	A °C	103	203	310	395	499	—	615	711	809	894	1002
	B	.000771	.00258	.00315	.00359	.00416	—	.00480	.00532	.00585	.00624	.00674
17	A °C	109	197	312	411	498	552	609	689	805	906	999
	B	.000537	.00164	.00202	.00247	.00296	.00325	.00361	.00409	.00460	.00508	.00550
18	A °C	103	199	310	395	505	—	605	696	795	900	1001
	B	.000437	.00121	.00172	.00217	.00281	—	.00351	.00392	.00438	.00487	.00531
20	A °C	105	198	307	400	495	557	612	701	795	904	988
	B	.000807	.00326	.00427	.00482	.00546	.00585	.00627	.00674	.00711	.00757	.00777
22	A °C	105	198	307	400	495	557	612	701	795	904	988
	B	.000711	.00169	.00215	.00256	.00306	.00340	.00383	.00416	.00455	.00479	.00507

TABLE III (*Concluded*)

A. Temperature at which expansion was determined, in °C
B. Observed expansion, per unit length, at temperature indicated.

Clay No.												
23	A °C	109	197	312	411	498	552	609	689	805	906	999
	B	.000709	.00208	.00295	.00350	.00407	.00450	.00537	.00572	.00604	.00635	.00647
25	A °C	109	197	312	411	498	552	609	689	805	906	999
	B	.000776	.00207	.00234	.00285	.00338	.00369	.00405	.00455	.00512	.00566	.00608
27	A °C	104	198	303	401	498	563	606	700	794	901	986
	B	.000806	.00222	.00284	.00349	.00410	.00467	.00519	.00566	.00604	.00646	.00675
28	A °C	106	195	299	398	496	555	604	699	805	909	999
	B	.000757	.00188	.00223	.00284	.00338	.00370	.00403	.00456	.00509	.00565	.00597
29	A °C	106	195	299	398	496	555	604	699	805	909	999
	B	.00070	.00224	.00303	.00360	.00431	.00475	.00533	.00576	.00613	.00643	.00662
30	A °C	103	203	310	395	499	—	615	711	809	894	1002
	B	.000615	.00184	.00253	.00300	.00369	—	.00518	.00556	.00592	.00617	.00651
31	A °C	110	209	300	401	504	556	604	704	790	893	1000
	B	.000688	.00162	.00200	.00246	.00297	.00325	.00362	.00411	.00449	.00498	.00539
40	A °C	108	206	311	401	512	—	605	705	795	893	991
	B	.000602	.00176	.00234	.00287	.00365	—	.00464	.00510	.00539	.00566	.00593
41	A °C	103	202	305	394	491	547	604	686	811	898	1000
	B	.000695	.00239	.00298	.00353	.00424	.00469	.00521	.00563	.00617	.00657	.00690
43	A °C	103	196	304	407	506	—	606	700	795	899	1000
	B	.000492	.00135	.00181	.00228	.00289	—	.00349	.00398	.00439	.00490	.00530
44	A °C	107	198	304	400	496	567	607	704	805	912	1002
	B	.000515	.00147	.00198	.00244	.00293	.00334	.00359	.00401	.00455	.00510	.00545
46	A °C	107	195	301	397	495	564	611	712	803	906	974
	B	.000616	.00153	.00208	.00257	.00318	.00367	.00449	.00483	.00506	.00529	.00536
48	A °C	107	195	301	397	495	564	611	712	803	906	974
	B	.000524	.00129	.00172	.00222	.00287	.00329	.00381	.00424	.00453	.00496	.00529
49	A °C	108	206	311	401	512	—	605	705	795	893	991
	B	.000625	.00181	.00232	.00287	.00354	—	.00453	.00496	.00536	.00572	.00614
50	A °C	114	188	310	395	511	—	606	700	801	900	1001
	B	.000694	.00180	.00249	.00295	.00353	—	.00456	.00505	.00550	.00597	.00640

from 500 to 600° and this can undoubtedly be attributed to the $\alpha \rightarrow \beta$ quartz inversion. For several clays the expansion from 500 to 550°, and from 550 to 600°, was also determined. For some clays the curves (Nos. 19, 46, and 48) showed plainly that the increased rate of expansion was restricted to the range 550–600°. Other curves (Nos. 2, 6, 23, and 27) showed equally plainly that the increase in rate of expansion started below 550°. This indicates that the inversions of quartz combined with clay may or may not take place (or at least appear to take place) within a rather definite temperature range, being

TABLE IV

DETAILED DATA GIVING THERMAL EXPANSIONS, AND TEMPERATURES AT WHICH OBSERVED, FOR CLAYS OF GROUP H

A. Temperature at which expansion was determined in °C.
B. Observed expansion per unit length at temperature indicated.

Clay No.												
15	A °C	103	194	314	409	511	—	604	704	795	879	988
	B	.000379	.000826	.00137	.00180	.00253	—	.00340	.00377	.00402	.00428	.00456
19	A °C	104	197	302	405	503	556	603	706	798	908	999
	B	.000440	.00122	.00175	.00230	.00296	.00325	.00429	.00476	.00495	.00522	.00536
21	A °C	105	198	307	400	495	557	612	701	795	904	988
	B	.000546	.00121	.00183	.00223	.00271	.00303	.00331	.00374	.00413	.00463	.00484
24	A °C	103	194	314	409	511	—	604	706	795	879	988
	B	.000588	.00113	.00160	.00200	.00255	—	.00339	.00385	.00418	.00460	.00492
26	A °C	119	200	304	407	511	—	608	701	794	894	1001
	B	.00047	.00099	.00150	.00208	.00278	—	.00398	.00434	.00456	.00487	.00523
32	A °C	120	207	307	412	523	—	612	702	790	903	989
	B	.000323	.000677	.00110	.00169	.00232	—	.00303	.00341	.00375	.00421	.00430
35	A °C	120	207	307	412	523	—	612	702	790	903	989
	B	.000357	.000769	.00115	.00167	.00222	—	.00288	.00326	.00364	.00420	.00459
36	A °C	103	196	304	407	506	—	606	700	795	899	1000
	B	.000373	.000839	.00132	.00187	.00252	—	.00327	.00374	.00426	.00495	.00542
37	A °C	103	199	310	395	505	—	605	696	795	900	1001
	B	.000367	.000954	.00167	.00225	.00304	—	.00391	.00439	.00496	.00572	.00629
38	A °C	106	194	313	391	505	—	628	705	795	897	993
	B	.000426	.000726	.00155	.00180	.00276	—	.00365	.00397	.00430	.00477	.00520
39	A °C	113	200	307	406	510	—	599	712	799	900	999
	B	.000429	.000840	.00137	.00176	.00220	—	.00276	.00339	.00363	.00399	.00431
42	A °C	98	197	313	400	495	544	605	705	808	904	997
	B	.000292	.00095	.00147	.00193	.00252	.00292	.00386	.00417	.00443	.00466	.00480
45	A °C	103	203	310	395	499	—	615	711	809	894	1002
	B	.000571	.00117	.00232	.00278	.00346	—	.00457	.00509	.00556	.00589	.00626
47	A °C	107	195	301	397	495	564	611	712	803	906	974
	B	.000393	.000881	.00131	.00179	.00238	.00279	.00326	.00369	.00405	.00460	.00495
51	A °C	103	197	307	392	501	557	605	700	798	910	996
	B	.000323	.000903	.00137	.00182	.00235	.00278	.00338	.00359	.00380	.00406	.00415

probably controlled by the previous thermal and geological history of the quartz and the clay of which it forms an integral part.

(f) From 600 to 1000°. The curves for many of the clays (Ex. 2 and 23) show a gradually decreasing rate of expansion as the temperature is raised from 600 to 1000°. In general this decrease in rate is proportional to the increased expansion between 500 and 600°, which may be the combined effect of expanding clay and contracting quartz[1] since there was no measurable decrease in the case of clays whose expansion curves indicated the absence of quartz.

The curves and data presented show many interesting relations, but it is evident that a more thorough understanding of their significance, particularly in the range from room temperature to 300°, will necessitate expansion determinations at less than one-hundred degree intervals. It might also be advisable to study synthetically prepared bodies containing known quantities of practically pure clay matter, tridymite, and cristobalite.

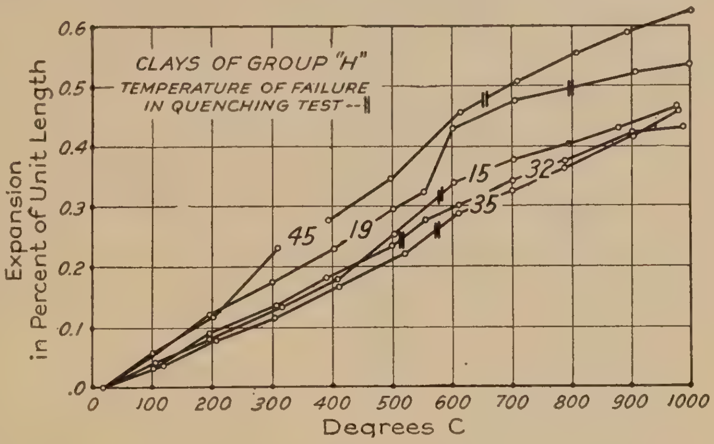

FIG. 8.—Thermal expansion curves of clays typical of Group H.

2. Expansion vs. Resistance to Failure in Quenching Test

While the quenching test referred to in the subtitle has been described in the first report[2] it might be well to outline again the method of procedure; five specimen saggers of each clay were air-quenched at progressively higher temperatures until fracture occurred. The initial furnace temperature was 350°C, the second 400°C, and for each succeeding test the temperature was increased 25°C until 800°C was reached. A satisfactory series of comparative results was obtained. It was found that a majority of the saggers fractured at or below 575°C. Saggers of one clay (No. 16), which is bauxitic, were still perfect at 800 and the test was continued to 1000°C, at which temperature no saggers had failed and the test was discontinued.

Of the forty-six clays submitted to the quenching test, thirty-two are of Group L (Table III) and fourteen of Group H (Table IV). With only five exceptions (Nos. 11, 16, 22, 23, and 30) all the clays of Group L failed in the quenching test *below* 500° while, of Group H, all the clays (one excepted, No. 37) failed *above* 500°; of these exceptions only three differ radically in their behavior from the rest of their group (Nos. 11, 16, and 23) for No. 22 failed at 505°, No. 30 at 510°, and No. 37 at 480°. There were, therefore, only three noteworthy exceptions to the rule that an increased rate of expansion from 100 to 200° decreases resistance to failure when suddenly cooled in air and, in the particular test used in this investigation, caused trial saggers to fail below 500° while others failed above 500°. The relation is brought out strikingly by the averages for the Groups as given in Table V. The data are given in detail in Table VI.

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[1] Previous investigators (C. N. Fenner, *loc. cit.*, and H. Insley, *loc. cit*) have shown that β quartz decreases in volume when heated above the inversion temperature.

[2] *Loc. cit.*, p. 138. This test was designed to simulate the sudden temperature changes to which a sagger is subjected when a kiln is opened and when the hot sagger is moved to the open air.

TABLE V

Group Averages

	Average temperature of failure in air-quenching test	Average porosity of specimens fired at 1230°C	Average expansion from 100° to 200°
	°C	%	%
Group L	436	31	0.139
Group H	606	24	0.057

While the average total expansion of clays of Group L, from room temperature to 1000°, is roughly 0.001 per unit length higher than that of Group H, it should be noted that this difference is caused by the greater expansion of Group L clays below 200°.

Whether the quenching test used in this investigation will determine the relative life of a sagger under plant conditions, or not, remains to be demonstrated. In any case it is believed that the relation between expansion from 100 to 200° and behavior in the quenching test is sufficiently definite to be of fundamental significance and worthy of consideration in connection with plant practice. In cooling a kiln it is generally considered safe to tear down the wickets after the kiln is "black" and permit the cooling to proceed as rapidly as possible, the argument being that the ware has safely passed the "quartz inversion"[1] and is therefore not liable to be harmed. The data presented here clearly show that there is not only a greater expansion from room temperature to 500° than from 500 to 1000°, but that for many clays the expansion rate may be very high at temperatures which are referred to as merely "warm" (100–200°). Furthermore it is indicated that the expansion behavior in this low range materially affects the life of the sagger. It would appear advisable then either to cool with greater care at these low temperatures, or to choose

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[1] The transition from a visible (low red) heat to an invisible (black) heat is naturally gradual but in practice is considered to take place at approximately 500°C. As previously stated, the $\alpha \leftrightarrows \beta$ quartz inversions occur at approximately 573.0°C.

TABLE VI

DATA PRESENTED TO SHOW THE RELATION BETWEEN MODULUS OF RUPTURE (COLD), TEMPERATURE OF FAILURE IN THE QUENCHING TEST, POROSITY, AND THERMAL EXPANSION BETWEEN 100 AND 200°

Clay No.	Group	Modulus of rupture of specimens fired at 1230°C Lbs. per sq. in.	Temp. of failure in air-quenching test °C	Porosity of specimens fired at 1230°C %	Expansion from 100° to 200° % per 1°C
1	L	2890	405	19.7	.00101
2	L	1570	445	34.1	.00118
4	L	1360	420	25.1	.00189
5	L	3165	370	15.7	.00122
6	L	734	410	35.0	.00170
7	L	1265	440	30.0	.00174
8	L	2420	405	32.2	.00147
9	L	2655	420	23.3	.00122
10	L	1980	420	22.3	.00199
11	L	1655	535	40.8	.00123
12	L	2165	400	25.5	.00145
13	L	1680	390	31.0	.00168
14	L	2277	390	29.3	.00145
15	H	3670	580	20.0	.00054
16	L	620	over 1000	39.0	.00211
17	L	2695	475	32.1	.00125
18	L	3650	405	20.4	.00080
19	H	1055	800	37.6	.00084
20	L	1380	400	32.3	.00264
21	H	2060	540	21.6	.00071
22	L	2490	505	27.4	.00105
23	L	615	580	30.2	.00156
24	H	3055	570	26.5	.00059
25	L	3290	495	27.7	.00147
26	H	2280	590	23.7	.00064
28	L	3090	415	22.8	.00126
29	L	2615	400	22.5	.00178
30	L	860	510	40.0	.00123
31	L	770	495	38.2	.00094
32	H	3225	515	10.1	.00041
35	H	3000	575	19.1	.00047
36	H	2910	545	13.0	.00050
37	H	5350	480	8.1	.00061
38	H	3060	535	21.8	.00034
39	H	3700	565	25.7	.00047
40	L	2510	400	32.6	.00098
41	L	3110	350	33.5	.00171
42	H	1500	745	27.6	.00067
43	L	2470	405	26.0	.00092
44	L	2525	490	27.5	.00105
45	H	3380	655	29.3	.00060
46	L	1105	435	38.0	.00102
48	L	3690	455	25.5	.00088
49	L	2300	460	27.6	.00121
50	L	2330	425	26.2	.00150
51	H	1055	770	23.5	.00062

sagger clays of minimum expansion and contraction[1] below 300°, *i.e.*, clays of the Group H type.

3. Effect of Porosity

The porosities of the specimens used in determining thermal expansion are given in Table VI and averaged, for the groups, in Table V. For the convenience of the reader they were also plotted (Fig. 9) against "temperature of failure in quenching test." Whether the relation indicated by Fig. 9 and the averages (Table V) are significant, or merely incidental to thermal expansion, is not known. However, it may be of interest that the resistance to failure in quenching *for clays of Group H* is roughly directly proportional to increase in porosity.

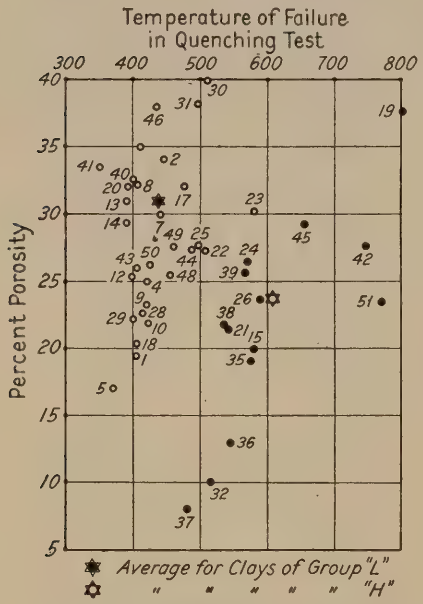

FIG. 9.—Showing the relation between porosity and temperature of failure in the quenching test. The data indicate that, for clays of Group H, the resistance to failure in the quenching test is proportional to porosity.

That this relation should exist for clays of Group H and not for clays of Group L can be accounted for by assuming that porosity becomes a factor only when no marked increase in rate of expansion takes place between 100 and 200° and, consequently, no "expansion strains" are introduced to overcome the effect of porosity. (The same assumption would hold with regard to the indicated relation between the modulus of rupture and resistance to failure in the quenching test for clays of Group H, see VI, 4.)

4. Effect of Fired Strength (Modulus of Rupture)

The moduli of rupture of the specimens used in determining thermal expansion are given in Table VI. It is indicated that the resistance to failure in quenching *for clays of Group H* is inversely proportional to strength (modulus of rupture). However, the relation is not as well defined as in the case of porosity (discussed above). The elasticity and modulus of rupture of the clays will be determined at the temperature of failure in the quenching test and it is believed that the information to be obtained in this way will have a more direct bearing on the problem of determining the influence of strength on the life of saggers.

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[1] The curves and data presented were obtained with rising temperatures, but it was demonstrated with clays of Group L that contractions with falling temperatures practically followed the same curves below 300°. A rising temperature was used because of the greater convenience in maintaining a definite temperature-time schedule.

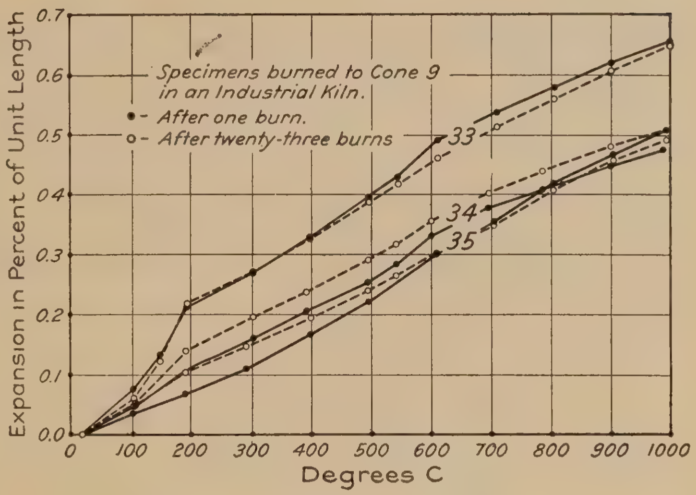

FIG. 10.—Thermal expansion curves showing the effect of repeated firings on thermal expansion. In general the data indicate that repeated firings lower the thermal expansion between 500 and 600° and increase the expansion between 100 and 200°.

5. Expansion as Affected by Repeated Firing

As stated in Section II, the composition and previous thermal history of the specimens used in this study are given in the first Progress Report, p. 141. In brief, the specimens were made of a mixture of 75% raw clay (or mixture of clays) and 25% grog of the same clay (or the same mixture of clays). Clays 11 and 12, and body 101 (an equal mixture of 11 and 12), were fired from one to seventeen times at cone 11. Clays 33, 34, and 35, and body 345 (an equal mixture of 33, 34, and 35), were fired from one to 26 times at cone 9.

The data (Table VII and Fig. 10) show that repeated firings lower the expansion between 500 and 600° and increase the expansion between 100 and 200°, indicating that the quartz initially present converts to another form of silica. In no case is there greater expansion from 200 to 300°, than from 300 to 400° to indicate the presence of cristobalite.[1]

Since repeated firings apparently tend to increase the 100 to 200° expansion, and since the data reported indicate this expansion to be a controlling factor in the life of saggers, it may be stated that,

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[1] H. S. Houldsworth and J. W. Cobb (*Jour. Amer. Ceram. Soc.*, 6[5], 645 (1923)) using an apparatus described by Boeck (*Trans. Amer. Ceram. Soc.*, **14**, 470 (1912)) observed an increased rate of expansion between 100 and 200° for Ayrshire bauxitic clay and Farnley fire clay, fired at cones 9 and 14, but not between 200 and 300°. The same phenomenon was noted by G. E. Merritt for Florida kaolin (Bur. Stand., *Sci. Paper*, No. 485, p. 368).

(*a*) the resistance of saggers to failure when subjected to sudden temperature changes can be expected to decrease with prolonged use no matter how carefully they are handled;[1] (*b*) the use of "old grog" (*i.e.*, grog obtained by grinding brick or saggers which have been reheated many times in the course of service) is detrimental since the possible structural changes evidenced by large expansion between 100 and 200° would be highly developed.

TABLE VII

THERMAL EXPANSION OF SPECIMENS FIRED IN COMMERCIAL KILNS

Clay No.	100°C to 200°C after 1 firing	100°C to 200°C after 17 firings	500°C to 600°C after 1 firing	500°C to 600°C after 17 firings
	%	%	%	%
11	0.127	0.161	0.060	0.053
12	0.154	0.167	0.073	0.065
101	0.150	0.160	0.060	0.047

Clay No.	100°C to 200°C after 1 firing	100°C to 200°C after 23 firings	500°C to 600°C after 1 firing	500°C to 600°C after 23 firings
33	0.155	0.181	0.083	0.063
34	0.070	0.102	0.073	0.061
35	0.036	0.065	0.075	0.055
345	0.065	0.115	0.068	0.061

6. Effect of Corundum on Thermal Expansion of Clay

The results obtained by determining the effects on thermal expansion of additions of artificial corundum to two sagger clays are shown in Figs. 11 and 12. For reference the thermal expansion of the corundum used was determined and is shown in Fig. 11.[2] The curves of clay No. 42 (curve 42, Fig. 11) and clay No. 25 (curve 25, Fig. 12) were plotted from the data given in Tables I and II. The mixtures used are given in Table VIII.

TABLE VIII

BODIES USED IN STUDYING EFFECT OF CORUNDUM ON THERMAL EXPANSION

Per Cent by Volume

Specimen No.	Clay No. 25 Raw	Clay No. 25 Calcined	Clay No. 42 Raw	Clay No. 42 Calcined	Corundum
25 A	50	25	—	—	25
25 B	40	—	—	—	60
42 A	—	—	50	25	25
42 B	—	—	40	—	60

The effect of the corundum is so evident from the curves as to require little discussion. Specimens of clay No. 42 (containing 70.2%

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[1] Data given in the first Progress Report (*loc. cit.*) on page 141 indicate that repeated firings will not decrease the transverse strength of sagger bodies at room temperature.

[2] The corundum and corundum and clay specimens were prepared by M. F. Beecher, of the Norton Company, using clays furnished by the Bureau.

SiO_2) underwent a slight increase in rate of expansion from 100 to 200° and a marked increase when heated from 540 to 600°. These irregularities were almost entirely removed by using 60% corundum (by volume) and greatly diminished by 25%.

Clay No. 25 (containing 54.8% SiO_2 after calcination) expanded very rapidly between 100 and 200°. By using 60% corundum (by volume) this excessive expansion was materially reduced.

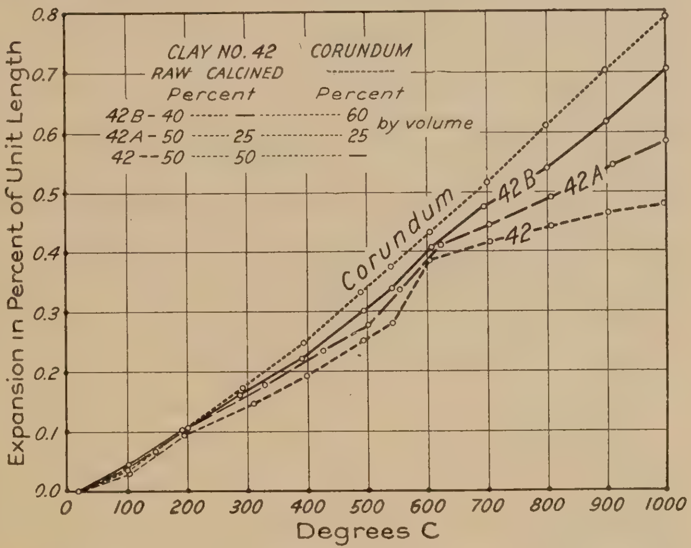

FIG. 11.—Curves showing the thermal expansion of clay No. 42, of mixtures of clay No. 42 and corundum, and of the corundum used in the mixtures.

Unfortunately the quenching tests were completed before these interesting results were obtained and consequently no data are available to show whether or not the mixture of clay and corundum having higher average, but regular expansions would be more resistant to sudden temperature changes than the clays alone.

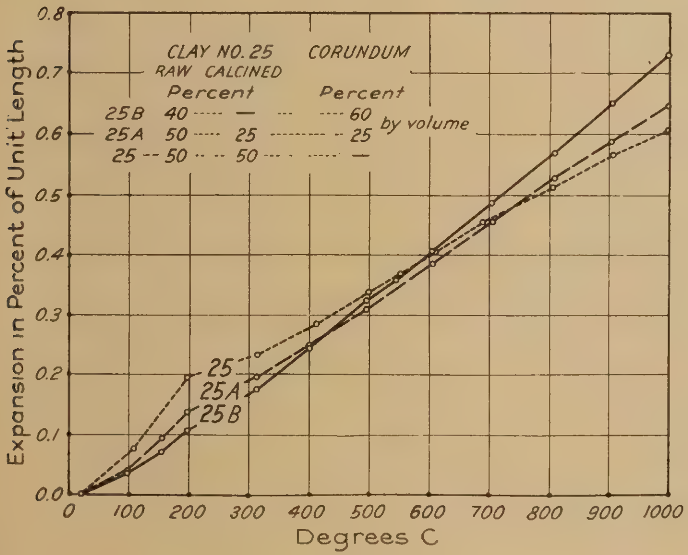

FIG. 12.—Curves showing the thermal expansion of clay No. 25 and of mixtures of clay No. 25 and corundum (the thermal expansion of the corundum used is shown in Fig. 11).

VII. Summary

This paper describes the results obtained with a relatively crude apparatus designed and constructed in the Ceramic Division of the Bureau of Standards for use in determining the thermal expansion of refractory clays and bodies, especially those used in the making of saggers.

The inversions of uncombined SiO_2 were sharply defined in some cases and barely discernible in others. A more thorough understanding of the significance of thermal expansion, particularly in the range from room temperature to 300°, will necessitate expansion determinations at less than 100°-intervals. It might be advisable also to prepare synthetically bodies containing known quantities of practically pure clay matter, tridymite, and cristobalite, for expansion studies.

There appear to be two distinct types of clays as regards thermal expansion and resistance to sudden temperature change. One (referred to in the paper as Group L) includes clays which expand very rapidly between 100 and 200° and crack or "dunt" below 500° in the air-quenching test; the other (referred to as Group H) includes clays of average expansion between 100 and 200°, and which fail in the air-quenching test at temperatures above 500°.

It was also shown that repeated firings tend to decrease the expansion between 500 and 600° and increase the expansion between 100 and 200°, indicating a resultant decreased resistance to sudden temperature change.

Supplementary tests of clay-corundum mixtures clearly showed that artificial corundum, while increasing the total average expansion of the clays with which it was used, tends to eliminate irregular expansion due to inversions of uncombined SiO_2.

FUSION POINTS OF FIREBRICK–COAL-ASH MIXTURES[1]

By L. C. Hewitt

ABSTRACT

Six types of refractory brick were tested with five types of coal ash, the cone fusion points of the brick-ash mixtures being determined over a range of 10% brick, 90% ash, to 40 % brick, 60% ash. A departure was made from previous methods in that high ash mixtures were studied rather than high brick mixtures, in the belief that boiler slags contain a relatively low proportion of the refractory. Sintered mixtures of refractory and ash tend to give higher fusion points than the raw mixtures do. Any determinations made in an uncontrolled atmosphere are exceedingly unreliable. The results obtained in this investigation indicate that the "cone-slag test" is of very limited value as a means of selecting refractories for boiler service.

Introduction

The laboratory tests conducted in this particular instance were prompted by a desire to study the merits of the "cone-slag test" as means of rating certain types of fire brick in respect to their ability to resist the fluxing actions of various coals as met in boiler practice.

In this investigation a departure is made from the methods heretofore employed,[2] in that a high ash or slag content mixture was taken as the starting point, with a gradually increasing brick content. This departure is based on the belief that the glass, resulting from erosion of fire brick by coal ash in boiler furnaces, must contain a low percentage of brick. The amount of ash deposited on the walls daily is ordinarily quite high. If all of the slag formed by the action of the ash with the brick contained even as much as 25% brick, the walls would last a comparatively short time.

All of the ash does not come in contact with the brick, but, on the other hand, an examination of the surface of the brick exposed to slag in a furnace wall usually shows a very thin coating of slag, indicating that erosion is usually on the surface, rather than by penetration of the slag, leading to the belief that the amount of brick dissolved would be low.

The proportions of ash and brick that react with each other in common boiler practice are shown in Table I.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division.)

[2] Previous reference in the *Journal of the American Ceramic Society* to the procedure of conducting the cone-slag test and the results obtained with certain mixtures have been given by Howe, *Jour. Amer. Ceram. Soc.*, **6,** 466–73 (1923); Howe, Phelps, and Ferguson, *Ibid.*, **6,** 589–95 (1923), and by Booze and Flint, *Ibid.*, **7,** 594–98 (1924); Kohlmeyer, *Ibid.*, **8,** 313–18 (1925) makes mention of it. Brennan in *Combustion*, June, 1924, in a study of "The Effect of Coal Ash on Refractories" also gives data on the cone fusion points of various brick-coal ash-mixtures.

TABLE I

CALCULATED PERCENTAGE OF BRICK IN BOILER SLAG

Analysis	Slag taken from Brick No. 2 Sample A%	Sample B%	Ill. Coal Ash 100%	Brick No. 2 100%	Calcd. proportion of ash and brick in slag Sample A%	Sample B%
Silica	49.46	52.00	49.44	57.52	100 ash 0.0 brick	70 ash 30 brick
Alumina	30.06	27.38	25.01	38.22	60 ash 40 brick	80 ash 20 brick
Iron Oxide	12.22	14.36	16.20	1.74	70 ash 30 brick	85 ash 15 brick
Titania	1.16	1.04	—	1.72	—	—
Lime	4.97	4.00	5.38	.31	90 ash 10 brick	75 ash 25 brick
Magnesia	.91	.92	—	.43	—	—
Alkalis	1.18	.95	—	.37	—	—

Slag Sample *A* represents a "stalactite" taken from the front wall of the boiler, and sample *B* represents a thin coating of slag of about $\frac{1}{16}$ inch in thickness, as taken from the sidewall brick. The data indicate that the glass resulting from erosion of fire brick by coal ash in boiler practice must contain a higher percentage of ash than brick; 40% brick content is the highest with the greater number under 25%.

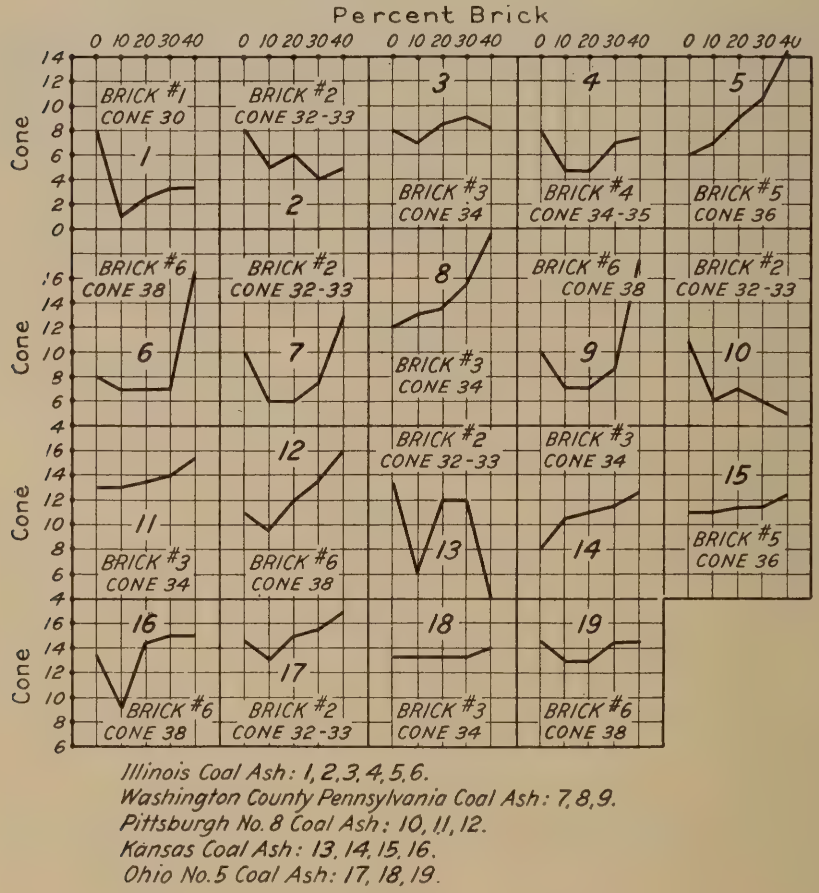

FIG. 1.

It has been thought there ofttimes is a tendency for some of the slag to melt out from the mixture before the chemical action between the brick and ash of a test cone has been completed. The tests, shown in Table II, were made to determine the effect of sintering the brick-ash mixtures before determining the fusion point. The mixtures marked "reheated" were heated at 1200°C for three hours before being fused.

In six of the nine cases given, the fusion point of the reheated mixture is higher than that of the raw mixture, and in the other three cases, the fusion points are equal, indicating that in the cone-slag test, as usually conducted, the slag tends to act alone causing a premature softening of the cone. This, at least, seems to be the case for the range tested, and, no doubt, it would hold true to a certain extent in high brick mixtures. These data are shown graphically in chart No. 43, Fig. 4.

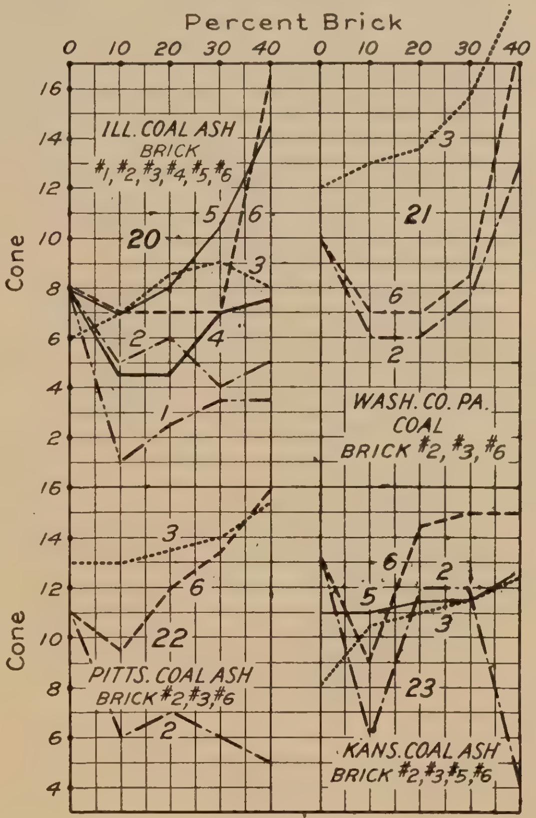

FIG. 2.

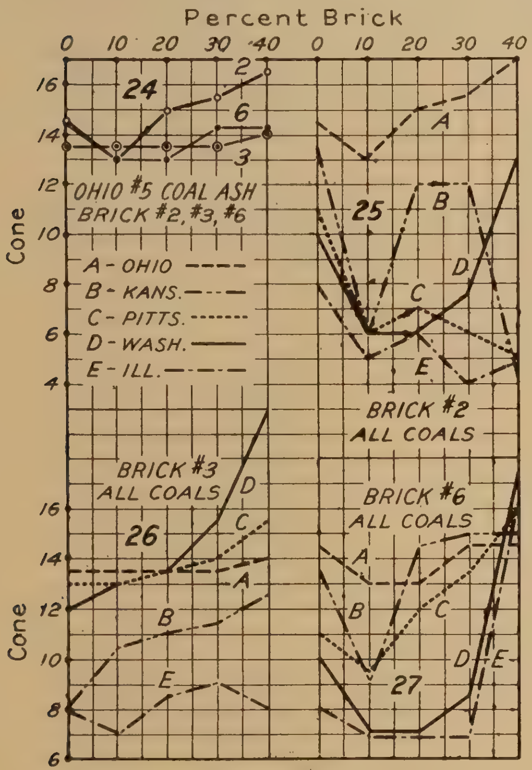

FIG. 3.

Brick-Ash Fusion Test Data

The Material Six brick, varying in in alumina content 32 to 75%, and five coal ashes, varying in iron content from 11 to 50%, were used. Samples of each brick were ground to pass 60-mesh. 50-pound samples of coal were secured from various mining sections. These were quartered to 5-pound lots, then to 3 pounds, the latter being fired in a clay crucible. The crucible was placed in a hot furnace at about 1000°C, and cooled down with free access of air. When coke formed, the sample was re-crushed and the oxidation process repeated. In all cases the carbon was thoroughly burned without sintering the ash.

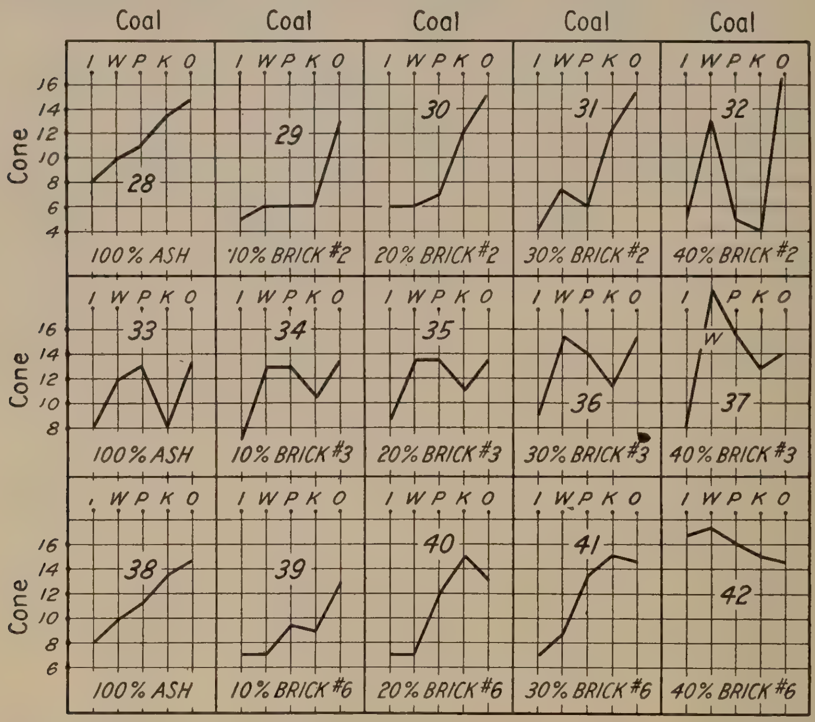

Fig. 4.

In the refractory-slag fusion tests made, bricks Nos. 2, 3, and 6 were the only brands tested with the ash of all coals included in this investigation, the two brands, Nos. 1 and 4, being used with the Illinois coal ash only, and brand No. 5 with the Illinois and Kansas.

Table II

Mixture	Fusion Point of Raw Mixture Temp. °C	Fusion Point of Raw Mixture Corresponding cone	Fusion Point of Reheated Mixture Temp. °C	Fusion Point of Reheated Mixture Corresponding cone
10–Kansas coal ash 90%	1330	10	1330	10
10–Pitts. No. 8 coal ash 90%	1250	6	1320	9–10
10–Wash. Co. Pa. coal ash 90%	1230	5	1280	7–8
10–Ill. coal ash 90%	1220	4–5	1260	6–7
20–Wash. Co. Pa. coal ash 80%	1250	6	1280	7–8
20–Ill. coal ash 80%	1220	4–5	1270	7
30–Pitts. No. 8, coal ash 70%	1300	8–9	1340	10–11
40–Kansas coal ash 60%	1350	11	1350	11
40–Pitts. No. 8 coal ash 60%	1370	12	1370	12

Table III

Fusion Points and Analyses of Coal Ash

	Illinois (inner group)	Wash. Co. Pa.	Pittsburgh No. 8	Kansas (Pitts. Dist.)	Ohio No. 5
Per Cent Ash	13.76	10.29	11.04	5.88	4.07
Fusion cone	6 and 8	10 and 12	11 and 13	8, 11 and 13–14	14–15
Silica	49.44	48.42	34.32	32.68	35.48
Alumina	25.01	29.51	12.22	20.82	28.08
Iron oxide	16.20	11.81	49.95	42.46	14.72
Titania	—	—	—	1.20	—
Calcium oxide	5.38	—	2.77	1.90	—
Magnesia	—	—	.34	.51	—
Alkali	—	—	.13	.91	—

Table III shows the per cent ash, fusion point, and chemical analysis of the ash as derived from the coals in question.

In Table IV is given the fusion point and chemical analysis of the

TABLE IV

FUSION POINTS AND ANALYSES OF FIREBRICK SAMPLES

	Brand No. 1	Brand No. 2	Brand No. 3	Brand No. 4	Brand No. 5	Brand No. 6
Fusion cone	30	32–33	34	34–35	36	38
Silica	63.44	57.52	49.60	42.04	29.84	17.58
Alumina	32.10	38.22	46.90	52.24	61.45	75.50
Iron	2.23	1.74	1.16	1.59	4.27	1.94
Titania	1.47	1.72	2.58	2.67	3.41	3.86
Lime	.32	.31	.15	.57	.32	.16
Magnesia	.06	.43	.34	.52	.13	.10
Alkali	.26	.37	.85	.77	.87	.55

Cone-Fusion Data on Mixtures

TABLE V

FUSION POINTS OF FIREBRICK–COAL-ASH MIXTURES

Brick	Illinois Coal Ash						Wash. Co. Pa. Coal Ash					
No.	100%	90%	80%	70%	60%	0%	100%	90%	80%	70%	60%	0%
1	8	1	2–3	3–4	3–4	30						
2	8	5	6	4	5	32–33	10	6	6	7–8	13	32–33
3	8	7	8–9	9	8	34	12	13	13–14	15–16	20	34
4	8	2–3	2–3	5	5–6	34–35						
5	6	7	9	10–11	14–15	36						
6	8	7	7	7	16–17	38	10	7	7	8–9	17–18	38

Brick	Pittsburgh No. 8 Coal Ash						Kansas Coal Ash					
No.	100%	90%	80%	70%	60%	0%	100%	90%	80%	70%	60%	0%
1												
2	11	6	7	6	5	32–33	13–14	6	12	12	4	32–33
3	13	13	13–14	14	15–16	34	8	10–11	11	11–12	12–13	34
4												
5							11	11	11–12	11–12	12–13	36
6	11	9–10	12	13–14	16	38	13–14	9	14–15	15	15	38

Brick	Ohio No. 5 Coal Ash					
No.	100%	90%	80%	70%	60%	0%
1						
2	14–15	13	15	15–16	17	32–33
3	13–14	13–14	13–14	13–14	14	34
4						
5						
6	14–15	13	13	14–15	14–15	38

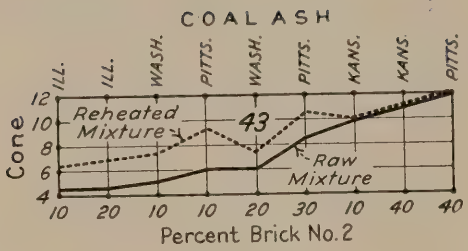

FIG. 4a

six brands of brick tested, these being listed in order of increasing alumina content.

In Table V is listed the cone-fusion figures on the various mixtures of ash and brick.

On Charts 1 to 19 inclusive are curves for the fusion points of each brick when mixed with various percentages of ash of the various coals. Charts 20 to 24 inclusive give a composite view of the fusion tests for each coal ash when mixed with varying percentages of the brick; charts 25 to 27 inclusive show composite curves for brick Nos. 2, 3, and 6, as tested with the different coal ashes, and charts 28 to 42 inclusive show comparison between the coal-ash samples when fused with various percentages of brick Nos. 2, 3, and 6.

Fusion Data on Ash Charts 20 to 24, and 28 and 33 show that the cone fusion of the same coal ash is not duplicated. Such a difference in the fusion of two samples of ash derived from the same 5-pound sample of coal, make it reasonable to expect a greater variation in tests on a coal ash at different periods, thus rendering the results of any one investigation of uncertain value in respect to any future application.

TABLE VI

EFFECT OF REDUCING CONDITIONS

Mixture		Fusion Points		
		Reducing Conditions		Oxidizing Conditions
Brick %	Ash % Kansas	°C	Cone*	Cone
40	No. 3— 60	1191	3	12–13
30	“— 70	1170	2	11–12
20	“— 80	1191	3	11
10	“— 90	1191	3	10–11
	“—100	1191	3	8
40	No. 5— 60	1309	9	12–13
30	“— 70	1233	5	11–12
20	“— 80	1216	4–5	11–12
10	“— 90	1204	3–4	11
	“—100	1174	2	11
40	No. 5— 60	1417	14–15	14–15
30	“— 70	1290	8	10–11
20	“— 80	1306	9	9

* Calculated.

Effect of Atmospheric Conditions

Fusion determinations were made on various mixtures under reducing conditions, in order to learn whether some of the seeming discrepancies or differences might be brought about from this cause. The reducing conditions were obtained simply by using a large excess of gas in the pot furnace when the fusions were made. The results are shown in Table VI.

The effect of reducing conditions is so marked as to make exceedingly unreliable any determinations made in an uncontrolled atmosphere. In actual boiler practice, the atmospheric conditions do, of course, change; if the cone-slag test is to be analogous with practice it must compensate for furnace conditions and this it does not do.

Effect of Iron Content

From the standpoint of rate of reaction and ease of erosion, we would expect the high iron ashes (Pittsburgh No. 8 and Kansas) to give the most pronounced results. This is not found to be the case, as is shown in charts 25 to 27. Kohlmeyer[1] of the Detroit Edison Company states, "The slagging action of coal ash is due to the iron content of the coal. This conclusion was reached after using coals having both high and low percentages of iron."

Effect of Alumina Content

Howe, Phelps, and Ferguson[2] found with 4 to 50% slag that the refractoriness of coal ash slag-refractory brick mixes increased with the alumina content of the refractory, though not in direct proportion. This was not found to be the case in this investigation, where the percentage of slag in the mixture varied from 60 to 90%. This is shown clearly in charts Nos. 20 to 24 inclusive, the brick having been numbered in sequence according to the alumina content, No. 2 having a higher alumina content than No. 1, etc. In these charts the brick arrange themselves in the following order in respect to fusion point, when heated under presumably oxidizing conditions.

Per Cent brick	Illinois coal	Wash. Co. Pa. coal	Pitts. No. 8 coal	Kansas coal	Ohio No. 5 coal
10	1,4,2,3, 5,6	2,6,3	2,6,3	2,6,3,5	2,6,3
20	1,4,2,6,5, 3	2,6,3	2,6,3	3,5,2,6	6,3,2
30	1,2,4,6,3, 5	2,6,3	2,6,3	3,5,2,6	3,6,2
40	1,2,4,3, 5,6	2,6,3	2,3,6	2,3,5,6	3,6,2

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[1] *Jour. Amer. Ceram. Soc.*, **8**, 317 (1925).

[2] *Loc. cit.*, p. 592.

General Observation

With the exception of the Washington County, Pennsylvania, coal-ash tests, the brick do not group themselves in any definite order. It is extremely difficult to draw any conclusions from the cone-slag test relative to comparative value of the refractories, for resisting coal-ash erosion. The fact that the fusion results may be altered entirely by a change in atmospheric conditions, and that eutectics form, and that reactions under various boiler conditions are not known, we are forced to conclude that the cone-slag test has very limited value in the selection of refractories to meet slag conditions in boilers.

With 50% and above of brick content, it would seem that the predominant factor in the fusion of brick-ash mixture, is the fusibility and alumina content of the brick itself (as found by Howe). This would apply strictly, however, only to fireclay refractories, other than those of very siliceous clays. It would be as logical to accept the comparative fusion points of the brick as it would be to accept the fusion points of high brick-ash mixtures.

Summary

The predominant ingredient of boiler wall slag is obviously coal ash rather than the refractory. The application of the cone-slag test to such mixtures develops that this test has very limited value as a means of rating the resisting qualities of refractories to coal-ash erosion in boilers,

(1) Fusion points on the ash from the same coal do not agree from time to time.

(2) Eutectics occur in fire brick–coal-ash mixtures. With no reliable data on the exact percentages of fire brick and coal ash that react with each other under actual boiler conditions, we have no standard guide of comparison.

(3) Any results secured in an uncontrolled atmosphere are exceedingly unreliable.

(4) The results secured do not coincide with practice inasmuch as the high iron ashes do not give the most pronounced results.

(5) The refractories do not group themselves in any defined order.

The author wishes to acknowledge the valuable suggestions made by M. C. Booze in this investigation.

Laclede-Christy Clay Products Co.
St. Louis, Mo.

MACHINE PRESSING OF TERRA COTTA[1]

By Robert Galbraith

ABSTRACT

A brief history and a description of the operation of the compressed air pressing machine are given. The manual operations as well as the costs are itemized. The machine requires 15½ men for its efficient operation, while the cost of pressing and finishing one ton of terra cotta is $5.85.

One of the chief factors contributing to America's leadership in wealth has been the development of labor saving machinery in all branches of industry. These machines have made it possible to produce a far greater amount of goods per man. The terra cotta industry has been one of the laggards in developing machine operations but it is, in this respect, rapidly changing.

One of the most glaring wastes of labor in terra cotta manufacture has been the hand pressing. Production in this department depends entirely on a man's arms and shoulders beating the clay in the mold until the piece is formed.

In 1916, M. E. Gates began a series of experiments which resulted in a machine which operates on the principle of an automobile cylinder. A mixture of gasoline vapor and air is introduced under pressure into a chamber and exploded with an electric spark. This explosion presses the clay against the sides and the face of the mold. While this machine operates satisfactorily, Mr. Gates felt that it could be improved; so in 1923 he designed the compressed air machine here described.

We believe the machine has been perfected until it is nearly in the final stages of its development. It has been in continuous operation for over a year with very few shutdowns resulting from mechanical failures. During the last six months there have been no shutdowns of a day's duration, while in the last three months only twelve hours have been lost. The last month has not seen an hour lost.

Description of Gates Pressing Machine

A diagram of the machine is shown in Fig. 1. The steel tank contains 180 cubic feet of air at an approximate pressure of 120 lbs. per sq. inch. This air is supplied by a 7 x 6½, single stage, simplate valve air compressor driven by a 25-horse power motor.

A small hydraulic piston pushes a mold onto the palette *A*, which palette is then raised by another hydraulic piston into the chamber *B*. This chamber will accommodate molds of maximum dimensions of 28 x 40 x 26 inches.

As soon as the palette closes the chamber, the firing rod raises a small trip valve, *C*, which releases the air holding up the large trip valve, *D*. This allows the valve to drop which releases the air between

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Terra Cotta Division.)

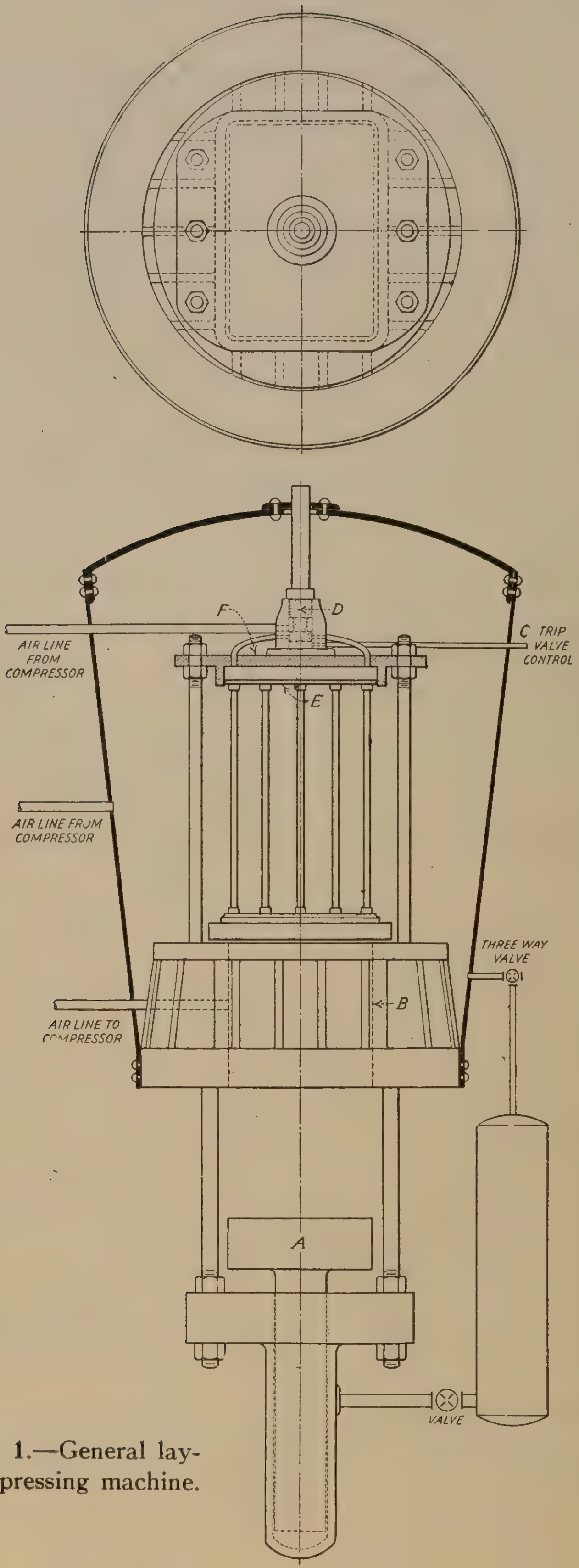

FIG. 1.—General layout pressing machine.

the two plates, *E* and *F*. When this air is gone, the unequal pressure raises the bottom plate which is directly connected to the valves below. When these valves are raised, the air in the tank rushes into the chamber with the speed of an explosion which presses the piece.

As soon as the mold is under pressure, the air compressor pumps the air out of the chamber back over the top plate forcing it down and seats the valves.

The chamber is then exhausted of its air upon which the piston valve releases and the machine is ready for the next mold.

The complete operation requires 36 seconds. With a larger compressor this time could be reduced. Figure 2 shows the mold on the palette ready for pressing.

Manual Labor Required A mold which has been blocked and dusted starts down the conveyor toward the machine. The first man cuts a piece of clay from his pile the size of the face and lays it in the mold. Then a man on each side of the runway puts in the sides and ends sealing their junction by raking it with their fingers. Another man then puts in the partitions, or webbing, while two men seal the cracks between the different parts of the mold with soft clay.

The molds are propelled by means of a walking conveyor consisting of a series of arms attached to eccentrics turned by a worm gear. These eccentrics give the arms the alternate motion of raising and going forward, then lowering and returning.

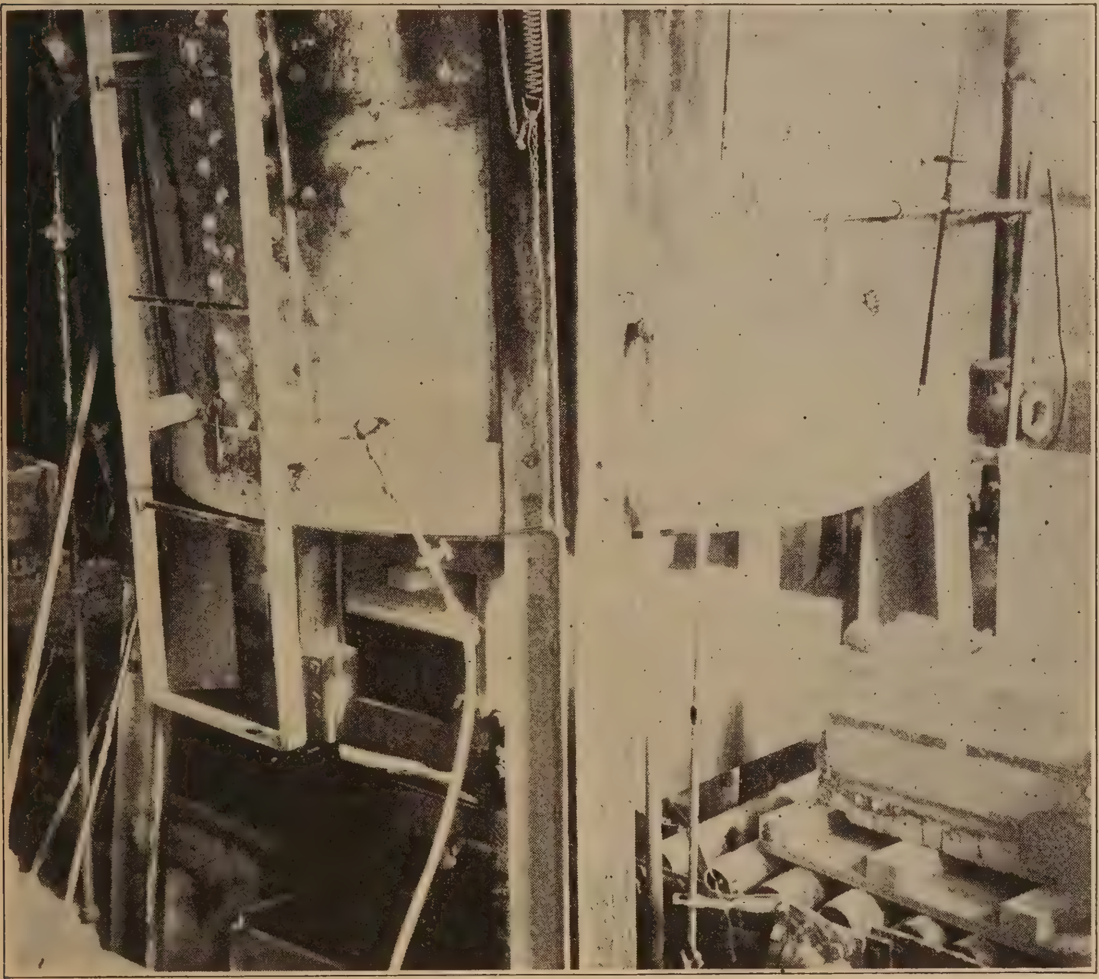

FIG. 2.—Mold on palette ready for pressing.

When a mold reaches the machine the piece is pressed, after which the excess clay is cut off the top and the inside of the piece is trimmed. High narrow molds are filled solid and the clay inside is dug out to form the partitions. Figure 3 shows same piece before and after pressing.

After rounding the curve, at the end of the machine, the mold goes on another conveyor which runs beneath a hot air pipe where, when it reaches the head end, the terra cotta is dried sufficiently to be dumped. Two men with the assistance of a small hydraulic piston dump the mold and replace the sides, ends, and face in their proper places. The band is then replaced and the mold blocked and dusted by the checker.

The piece of terra cotta is placed in a steel rack which has a capacity of twenty pieces. This rack is then moved to the finishers with a lift truck. After finishing, the pressing operation is considered complete and the racks are trucked to the driers.

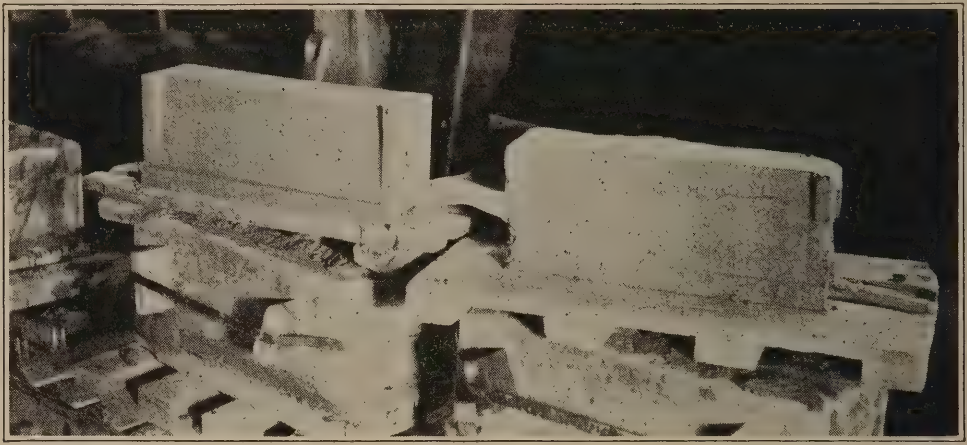

FIG. 3.—Same piece before and after pressing.

Labor Involved

A summary of the labor involved in the operation of the pressing machine gives the following:

One man putting in faces
Two men for sides and ends
One man for partitions
Two men sealing the mold
One man operating the machine
One man trimming the inside of the pieces
Two men dumping molds
One checker
One offbearer
Three finishers
One-half a trucker; one man trucks for two machines
One foreman in charge of both machines

This gives a total of 15½ men. The word "man" has been used here rather ambiguously as they are really boys of 17 and 18 years of age. They produce just as much terra cotta as men and are satisfied with a lower wage.

Cost of Operation

We have no figures of our own for a comparison of the cost of hand and machine pressing. Machine pieces range in size from 0.254 to 1.02 cubic feet. The average is 0.524 cubic feet while the average weight is 42 lbs.

Itemizing the cost of machine pressing gives the following:

Number of pieces pressed per man per day	33.33
Tons of terra cotta pressed per man per day	.729
Average daily wage per man	$4.10
Operation and maintenance per day	$5.00
Cost of machine pressing one ton of terra cotta	$5.85

AMERICAN TERRA COTTA AND CERAMIC CO.
TERRA COTTA, ILL.

SOME SOURCES OF AIR IN CLAY COLUMNS[1]

By S. L. Galpin

ABSTRACT

Absorbed gases are of considerable importance as sources of air in clay columns. A few measurements are reported, and inferences drawn thereon.

The air commonly present in green clay wares, and so often a trouble maker in clay columns is usually attributed to trapping of part of the air filling spaces between the fragments of crushed clay or shale used. While this source of air is no doubt responsible for much of that present in tempered clay, it seems probable that there is another source of some importance.

It is known that many substances, when finely divided, adsorb considerable quantities of gases. A simple experiment has been used to demonstrate that this property is also possessed by clays and shales to such an extent that its consideration as a source of air is worth while. When water is mixed with dry or partly dry clay it has the power to replace the air (or gas) films adsorbed or compressed upon the clay particles. The expansion of the air or gases released is proportional to the change of pressure resulting.

To measure this expansion of released gases, a weighed amount of clay is placed in a stoppered bottle (*S* Fig. 1). A measured amount of water is admitted from funnel, *A*. The change in volume of adsorbed air as it is released and expands, can then be seen and measured in a gas burette, *B*.

Results of some experiments with different clays are indicated on Fig. 2. The figures have been corrected for temperature changes, and the gas expansion calculated in per cent of clay volume.

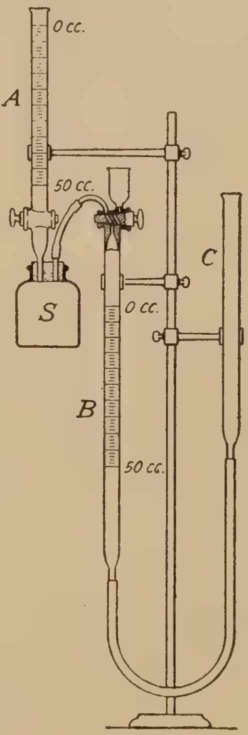

Fig. 1.

With the exception of tests with one shale, the results are in general similar. Expansion of the air-water-clay system starts directly after water is added to clay. Probably none of the runs was carried to the point of complete air release as examination of the clay residues showed in each case a considerable number of hard, partly slaked lumps. The decrease in volume of the air-water-clay system, during the first few seconds of tests with Canton, Ohio, shale is possibly due to the compression of pore air by the water film advancing into the clay grains. The decrease stops when internal pressure disrupts the bonds holding the clay particles together.

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[1] Presented by permission of the Director, Engineering Experiment Station, Iowa State College. Read at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Heavy Clay Products Division.)

The following statements concerning adsorbed air in clay seem warranted:

(1) Air-dried clay contains considerable amounts of adsorbed gases. (Whether clay adsorbs certain gases of the air in preference to others has not been determined.) These gases, when released from the compressing effect of adsorption may have a volume greater than that of the clay which contained them. A given clay will adsorb a greater percentage of permanent gases from dry than from humid air. Clay that has been wet for a long time probably contains no free air, although there may be air in solution.

(2) Adsorbed air may be driven from the surface of clay particles by water films. When just enough water is added to coat the clay particles the air may be largely adsorbed upon the water surfaces. When there is excess water in the clay the gases are released in proportion to reduction of adsorbing surface. The extent to which the released gases expand depends upon the confining pressure of the clay mass. With an excess of water some clays yield important amounts of adsorbed gases within three to five minutes after wetting. Others may require several hours to show appreciable change. In the making of some wares release may continue after shaping has been completed, with resulting swelling and loss of cohesion.

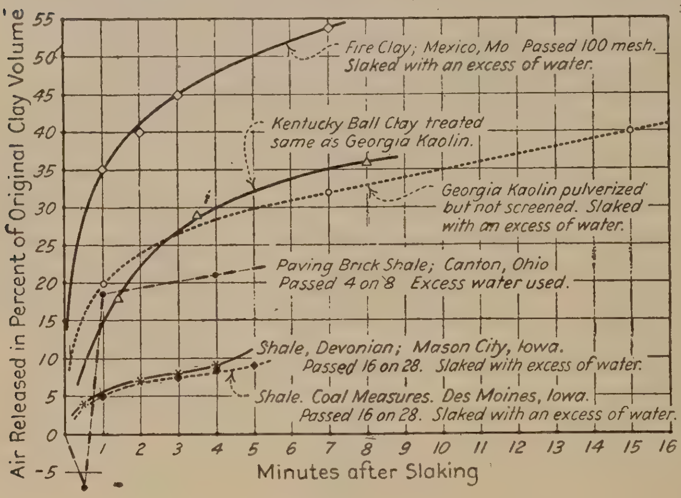

FIG. 2.

Where only sufficient water is added to clay to yield stiff-mud consistency little adsorbed air escapes from the mass. Probably but part of the adsorbed air is released due to incomplete wetting. Such as is freed exists, if the clay is undisturbed, in minute bubbles.

(3) Agitation of clay with water hastens the release and expansion of adsorbed air by aiding penetration of water and by coalescing bubblets.

(4) Removal of adsorbed air from clay is difficult even when an excess of water is used. Blunging followed by aging seems most effec-

tive since blunging releases the larger bubbles and aging allows the removal of the minute ones through solution. Processes of tempering which cannot be expected to remove adsorbed air, should operate best when as little release and collection of bubbles as possible is caused.

(5) Alternate wetting and drying is an effective method for softening and fining clays and shales.

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PRACTICAL CHEMICAL CONTROL OF PICKLING ROOM SOLUTIONS[1]

By B. T. Sweely

ABSTRACT

This paper gives a brief outline of pickle room practice, and gives in detail a rapid method of titration of solutions by use of especially graduated cylinders and the addition of indicator to normal or fractionally normal solutions.

Chemical control of the strengths of the solutions used for cleaning, pickling, and neutralizing in the enamel industry, is essential if the best results are to be obtained. The methods and data submitted below are the results of several years' experience, and have proven practical and economical.

It might be well to observe at the outset that extreme accuracy is not attained by these methods, but since a variation of from 1 to .5% in acid solutions has but little effect on the pickling process, we have found these methods sufficiently accurate to control shop operations, and so simple and rapid that the pickle room foreman can test his solutions twice a day with no loss of time or production.

The pickle room practice at our plant is, briefly, to pack the ware in monel baskets and put it through the successive steps of cleaning, rinsing, pickling, rinsing, and neutralizing. After neutralizing, the basket of ware is set on a car and passed through a tunnel drier, after which it is ready for the dipping operation. No hand labor is used beyond loading the ware into the baskets and unloading it after it leaves the drier.

The control of the strength of the solutions used in the cleaning, pickling, and neutralizing operations, is a simple problem to the chemist, but our purpose was to so simplify it as to make it easy for the shop man to keep his solutions under definite control.

In testing the strength of the solutions, we have used normal or fractionally normal solutions of acid and alkali. For testing the cleaning solutions, a normal sulphuric acid solution is used; for testing the acid bath, a half-normal sodium hydrate solution is used; and for testing the neutralizing baths, we are using a tenth-normal sulphuric acid solution. These solutions, of the strength desired, may be purchased from any drug or chemical supply house, or, of course, can be made up as required.

Methyl orange is used as an indicator, as it gives a fairly sharp end point even in the presence of ferrous hydrate or CO_2 gas. This indicator is added to the standard solution when ready for use.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb. 1926. (Enamel Division.)

In determining the strength at which we wished to maintain the solutions, we neglected the actual weight of a cubic centimeter and assumed the per cent by weight of acid or alkali present was the grams per cc. shown by titration, *i.e.*, a normal NaOH solution containing .04008 gms. NaOH per cc. was considered a 4% solution. Obviously this method does not give per cent by weight of acid or alkali present, but the number of grams of acid or alkali present in each cc. of solution.

The strength of the baths we have found best suited to our solutions and working conditions are as follows:

	Per cent
Cleaning solution	3–5
Acid solution (sulphuric)	3½–5
No. 1 neutralizing bath	.6–.8
No. 2 neutralizing bath	.15–.20

Having determined the approximate strengths at which we wished to maintain the various baths, we modified the usual method of titration to meet the requirements for shop use, by putting the indicator in the standard solution and using a cylinder graduated to fit the job.

In testing for acid strength, we have graduated a cylinder at 10 cc. and in divisions of two cubic centimeters, up to 28 cc. The $\frac{N}{2}$ NaOH solution, colored by the methyl orange indicator, is placed in a half-gallon bottle, tightly stoppered with a siphon and pinch cock attached. The operator fills the graduate to the 10 cc. mark with acid from the pickling tank, and runs in the half-normal alkali until the color changes, then reads the grams of acid present in each cc., or per cent as above, direct from the divisions on the cylinder.

Since each division above the 10 cc. mark is 2 cc., and we are using a half-normal alkali to neutralize 10 cc. of unknown H_2SO_4 solution, it follows that each division above the 10 cc. mark represents approximately one-half gram of acid present in the 10 cc. sample. If therefore, the 10 cc. sample consumes less than 6 divisions (12 cc.) of alkali, the pickling solution is too weak and more acid is added to the bath; if more than 10 divisions (20 cc.) of alkali are required to change color, the pickling solution is too strong and water is added to dilute the bath to the proper strength. Continued use of this test develops the judgment of the operator to the point where it is really surprising how accurately he will estimate the amount of acid or water required, as the case may be, to bring the strength of the bath within the limits fixed for his guidance.

The same procedure is used in testing our cleaning and neutralizing solutions, but a different scale of graduations is used. These cylinders are graduated at 10 cc. and the following divisions are marked at

$2\frac{1}{2}$ cc. up to 10 divisions. The change in the scale is necessitated by the difference in molecular weight of the acid and alkali, that of sulphuric acid being approximately 50, while that of sodium hydrate is about 40. Since we wish to read in terms of 1% or 1 gram per cc., it is obvious the graduation must be in the necessary multiple of the molecular weight.

The standard solution used for testing and cleaning solution is a normal H_2SO_4 solution with methyl orange indicator added, and placed in a stoppered bottle as described above. The 10 cc. sample is placed in the graduate and the normal acid run in until there is a distinct color change as before; if less than three divisions ($7\frac{1}{2}$ cc.) are required to change color, the bath is too weak and more cleaning compound is added; if more than 5 divisions ($12\frac{1}{2}$ cc.) are required, the bath is too strong and must be diluted.

The neutralizing baths are tested in exactly the same manner, except that an $\frac{N}{10}$ acid is used in order to secure greater accuracy, and to permit the use of the same cylinder as is used for the cleaning solution test. That is, since limits of alkalinity are from .15 grams to .20 grams NaOH per cc. for the last tank, and from .6 grams to .8 grams per cc. for the first tank, we are working with concentrations only one-tenth as great as are those used in the cleaning operation, and consequently use a standard solution of only one-tenth the strength.

In testing these solutions therefore, a sample of 10 cc. from the last tank is placed in the cylinder, and the $\frac{N}{10}$ acid run in until the color changes. Should this require less than one division (2.5 cc.) the bath is too weak and more compound must be added; if more than two divisions are required (5 cc.) the bath is too strong and must be diluted.

Likewise for the first neutralizing tank a 10 cc. sample must consume at least 6 divisions (15 cc.) of the tenth-normal acid or the bath is too weak and if more than 8 divisions (20 cc.) is necessary to change color the bath is too strong and must be diluted,

The above sums up what we have found to be a rapid and practical method of keeping our solution strengths under control. As stated at the outset, great accuracy is not secured nor is it necessary, as changes of 1 to $1\frac{1}{2}$% in strength of the solutions will be encountered daily, due to exhaustion by the work handled, but it has enabled us to keep the baths within limits that we have found will give us satisfactory results.

Baltimore Enamel and Novelty Co.
Baltimore, Md.

THE THEORY OF CLEANING OF SHEET IRON AND STEEL FOR ENAMELING PURPOSES[1]

By Homer F. Staley

ABSTRACT

Cleaning may be done by sand blasting, heating, use of solvents, or use of alkaline solutions. Of these methods, heating and use of alkaline solutions are important at present. In cleaning by heating the best results are obtained when the articles are first dipped in a solution of acid, heated uniformly to the lowest temperature that will cause the oils and greases to be burned off, and cooled slowly, both heating and cooling being done with the admission of as little air as possible.

In cleaning by the use of alkaline solutions, saponifiable oils are removed by the formation of soaps and the subsequent solution of these; non-saponifiable oils are removed by emulsification. Efficient cleaning depends primarily on the choice of cutting and drawing oils so as to have present a proper ratio of saponifiable and non-saponifiable oils. The cleaning solution must vary in composition according to the kinds and amounts of oils to be removed.

In the process of manufacturing black shapes for enameling from sheet iron and steel, they become more or less coated with greases and oils. These may be fats and greases used to prevent rusting while the stock is being shipped or is in storage, or oils used in cutting and drawing operations.

In order to avoid trouble in subsequent operations, it is essential that all traces of these oils and greases be removed before the shapes are subjected to "pickling." The process of removing these oils and greases is known in enameling technology as cleaning. The following methods are available: (*a*) sand blasting, (*b*) heating, (*c*) use of solvents, and (*d*) use of alkaline solutions.

Sand Blasting

The use of the sand blast is almost universal for cleaning cast iron for enameling. For fairly large pieces of simple shape it is quick and economical and has the advantage of removing not only oils and greases but also oxide of iron and scale. Therefore, it takes the place not only of the cleaning but of "pickling" operations. However, on account of the high air pressures employed in the commonly used type of sand blasting apparatus, the mechanical action is too severe for thin sheets causing too much abrasion and warping. The sand blast is used to advantage for cleaning steel shapes made from heavy plates for chemical apparatus.

There is no inherent reason why a sand blast apparatus operating at low pressures should not be devised for the cleaning of large thin pieces of sheet metal in simple shapes such as stove parts, signs, and

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[1] Received June 18, 1926.

refrigerator linings. If, as is the case, it is possible to clean eggs by sand blasting it should be possible to clean thin steel shapes.

Cleaning by Heating

Cleaning by heating, commonly called "scaling," consists essentially of heating the ware to the temperature at which the oils and greases are volatilized or take fire and burn off. At the same time the outer layer of metal is converted to iron oxide and many of the strains set up in the metal during rolling, stamping, and spinning are relieved due to the annealing action in the furnace.

Since the formation of a heavy layer of oxide during the scaling operation is a decided detriment in the subsequent pickling operation, the process should be conducted in such a manner as to form the least amount of scale and to have this as loosely adherent as possible. The best results are obtained when the articles are first dipped in a solution of acid, are heated uniformly to the lowest temperature that will cause the oils and greases to be burned off and are cooled slowly, both heating and cooling being done with the admission of as little air as possible. The acid dip serves to partially loosen any heavy scale present and to cause the oxide formed during the heating operation to be fine grained and easily removable.

Use of Solvents

All oils, fats, and greases are readily removed by the use of solvents. The materials most available are benzol, kerosene, gasoline, and alcohol. Owing to the high cost of the solvents, the difficulty of recovering them and the fire hazards involved in their use, they are not used for cleaning enameling shapes. Occasionally a spot of grease or oil that has gotten onto a piece by accident is removed by swabbing it with a rag dipped in gasoline or kerosene.

Use of Alkaline Solutions

The commonly used chemical method for the removal of oils and greases consists in the use of alkalis in water solution or of substances which on dissolving in water give alkaline solutions. The alkaline salt need not be caustic soda or potash. Salts of weak acids which hydrolize and give alkalis may be used. Caustic soda, however, is the most effective, part for part, with trisodium phosphate, soda ash, sodium silicate, and borax following, arranged in the order of their efficiency.

In many cases the alkalis act as water softeners and hence hard water must be avoided because the alkalis are partly wasted and likewise form soaps or insoluble gummy materials which may be deposited on the ware.

Classes of Oils and Greases

With reference to their action with alkaline solutions, oils and greases may be divided into two groups.

1. Saponifiable oils and greases. These contain "fatty acids" which combine chemically with alkalis in solution to form soaps. They are of either animal or vegetable origin. They are also known as "fatty oils," which distinguishes them from both the mineral oils and the non-saponifiable animal and vegetable "essential" oils.

2. Non-saponifiable oils and greases. These contain no fatty acids and consist of mineral oils, essential animal oils, and essential vegetable oils.

A definite distinction must be made between the action of alkaline cleaners with saponifiable oils and their action with oils that are not saponifiable.

1. Saponifiable Oils When saponifiable oils, fats and greases occurring on the ware are brought into contact with alkaline solutions they first undergo emulsification and then saponification. That is, they finally form soaps.

Emulsification consists of the formation of a suspension of one liquid in another in the form of very minute drops. In this case, when the alkaline solution comes in contact with the oil or grease the first action is the dissemination of the oil in small drops throughout the liquid. This effect is purely one of surface tension.

Next there is a chemical action between the fatty acid in the saponifiable oil and the alkali in the solution which results in the formation of a soap. As most alkaline soaps are soluble in water, the soap dissolves leaving the surface of the metal clean. Heating the solution aids in the formation of the soap and in its subsequent solution.

Saponification of the fatty oils not only serves to remove these oils from the ware but also aids in the removal of other oils and dirt due to the action of the soap formed. Soap aids in the formation of emulsions of the non-saponifiable oils and also in the removal of particles of grit by taking them into suspension. The latter action is due to the circumstance that soap solutions have very low surface tensions. Therefore, when they envelop a particle of grit, the force with which the grit adheres to the surface of the ware is lessened, and the particle floats away or drops down into the bath. While the cleansing action of soaps is well known, it would be quite expensive to clean large quantities of ware by the use of regularly manufactured soaps. In this case, where there is present on the ware oils containing fatty acid, one of the two chief ingredients of soap, it is quite logical to add alkali, the other chief ingredient, and to actually manufacture soap in the cleaning bath. In cases where large amounts of grease and oil are to be removed and there is little or no saponifiable matter present, both alkali and fatty acid (generally in the shape of rosin) may be added to the bath with advantage. A disadvantage in the formation of too much soap is that it is difficult to rinse it from the ware.

2. Non-Saponifiable Oils With non-saponifiable oils and greases, the first action of the alkaline solution is the same as in the case of the saponifiable oils. That is, an emulsion of oil in water is formed. Then the globules of oil gradually rise to the surface of the bath and coalescing, form a layer of oil on the surface.

This sounds very simple, but in actual practice it is very difficult to clean metals by emulsification of non-saponifiable oils by alkaline solutions alone. The emulsions do not form readily and are not stable; that is, they break down easily. Moreover, the globules of oil do not separate from the surface of the ware but adhere to it tenaciously.

The stability of the emulsion is dependent on the relative amounts of solution and oil, and on the amount of alkali in the water, or as it is at present fashionable to say, on the hydrogen-ion concentration. The greater the proportion of solution to oil and the stronger the solution is in alkalinity, the more stable the emulsion becomes. However, the greatest aid to the emulsification of non-saponifiable oils is the addition or production of a relatively small amount of soap. When any saponifiable oil is present, soap is produced automatically as explained above. Otherwise, soap or soap-forming ingredients may be added to the bath. Soap makes the emulsion more stable, preventing the breaking down of the emulsion as fast as it is formed and at the same time acts on the globules of oil in the same way that it acts on particles of grit, loosening them from the surface of the ware, thus permitting them to float to the surface of the bath. While a little soap is a great help, too much soap is a detriment since it makes the emulsion so stable that it will not break down at all so as to allow the oil to separate at the surface of the bath.

Another method of increasing the stability of emulsions is to add to the bath some solid so finely divided that the particles are colloidal in size. Their action is purely mechanical. Agitation of the bath either by passing into it steam or air or by stirring greatly aids the separation of the emulsified oil from the surface of the ware. Quite often inert materials of size larger than colloidal are added to produce a scrubbing or scouring action when the cleaning solution is circulated past the objects to be cleaned.

Electrolytic Cleaning

In addition to the regular alkaline solutions there is also employed electrolytic alkaline cleaning. This method is growing more and more popular due to the decrease in the time required and the effectiveness of the cleaning. The concentration of the alkali solution used is usually about the same as in the method described above, about the only requirement being that the alkaline solution should be of high conductivity.

The articles to be cleaned are made the cathode and an iron anode is used or the iron cleaning tank is used as anode. The principle cleaning action results from the production of finely divided gases which lift off the oil or grease film and assist in its emulsification or saponification. This gas evolution likewise aids the stirring of the solution which continually brings fresh solution to the cathode surfaces.

Choice of Oils and Cleaners

From the foregoing discussion it is evident that there is no such thing as a "good cleaner for all sorts of work." For effective work the composition of the cleaner must be fitted not only to the amount of oils and greases present but particularly to the relative amounts of saponifiable and non-saponifiable oils.

Insofar as possible, drawing and cutting oils should be chosen with consideration to the ease of subsequent cleaning. If saponifiable oils are used exclusively, too much soap will be produced in the cleaning operation. On the other hand, if non-saponifiable oils are used alone, it will be difficult to emulsify them due to the absence of soap. The best combination of oils from the standpoint of subsequent cleaning is one which contains sufficient saponifiable oil to give the proper amount of soap to cause a fairly stable emulsion of the non-saponifiable oils.

If the combination of oils used gives too much soap, the obvious thing to do is to see that the cleaner contains no soap or ingredients containing fatty acids, such as rosin. If this is not effective the proportion of saponifiable oils should be reduced.

If the combination of oils used gives too little soap, recourse can be had to the use of some soap or rosin in the cleaner, but a more satisfactory plan would be to increase the proportion of saponifiable oils used.

By devoting a little study to the action of his cleaning solutions, particularly with the aid of a few test tubes and a low-power magnifying glass, the plant superintendent can determine whether his solution is too rich or too poor in soap, and change his oils or his solution accordingly.

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A SIMPLE "SEALED-IN MERCURY ELECTRODE" APPARATUS FOR TESTING THE BREAKDOWN VOLTAGE OF HEAVY INSULATING MATERIALS[1]

By Louis Navias

ABSTRACT

A method has been developed whereby thick plates of insulating materials (of small area) may be electrically punctured under oil. The specimen is cemented between two hollow electrode holders by means of red sealing wax, as illustrated. One electrode holder, the elbow, may be made of ordinary cast-iron piping or glass. Mercury poured into both tubes gives the necessary contact. It is possible by these means to puncture a porcelain cylinder of diameter 1⅛ inches and 1⅛ inches thick at 142 kv., and with a porcelain cylinder 2 inches in diameter and 2 inches thick to reach 176 kv. without arcing. The "sealed-in mercury electrode" method has been compared with two other methods employing spheres and disks as electrodes, by puncturing cast polished plate glass specimens. The new method gives consistent results, the values being on the average 15% higher than values obtained by the other two methods.

Dielectric Strength Test Specimens in Experimental Use

In plant control work it has been found expedient to use some manufactured shape, as an insulator, usually with the standard (metal) hardware attached and to determine the puncture voltage on the assembled article. The result is a composite one and serves to indicate the limits to be found in a simulative service test.

For purely experimental work a number of shapes of porcelain specimens have been advocated and used. A few of these are here indicated. Radcliffe[2] made shallow dishes by the jiggering process, 2⅞ inches diameter across the top, 1 inch deep, with a bottom thickness of from 1.4 to 7 mm. The bottom was punctured in oil between two small-diameter electrodes. Weimer and Dun[3] made use of a cylindrical test cup 5¼ inches high, 3 inches diameter, and 0.15 inch thick. Electrical contact was made on both sides of the bottom with metal electrodes. It is here assumed that the walls and bottom were uniformly thick.

In their experiments on electrical resistivity Honeman and Fonseca[4] used a cylindrical cup 6.5 cm. high, 6 cm. diameter and a bottom 2.5 mm. thick. Their illustration shows a uniform thickness for wall and bottom with sharp corners between the two.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb. 1926.

[2] B. S. Radcliffe, "Investigations on the Dielectric Strength of Some Porcelains," *Trans. Amer. Ceram. Soc.*, **14**, 575–91 (1912).

[3] George Weimer and C. T. Dun, "The Effect of Temperature on the Dielectric Strength of Porcelains," *Trans. Amer. Ceram. Soc.*, **14**, 280–91 (1912).

[4] R. K. Honeman and E. L. Fonseca, "Electrical Resistance of Various Insulating Materials at High Temperatures," Report 53, of the National Advisory Comm. for Aeronautics, pp. 15–23 (1920).

The American Society for Testing Materials in 1924 had two shapes for insulating materials. The "Standard Method for Testing Molded Insulating Materials," D 48–24, requires a cup 2½ inches high, 2¼ inches overall diameter, with a central portion of the bottom about 1⅜-inch diameter and 5 mm. thick. The inner wall is tapered from the bottom to the top, where the wall is only ⅛ inch thick. Mercury is poured into the cup and the cup itself is floated on mercury to give the two electrodes.

Under the heading of the "Tentative Methods for Testing Electrical Porcelain," D 116–24 T, the American Society for Testing Materials requires a cylindrical tube, 12 inches long, of internal diameter 1¼ inches, and external diameter 2¾ inches, giving a ¾-inch wall. The center of the tube on the outside is grooved, radius 1½ inches, giving a minimum section of porcelain ½ inch thick through which the puncture occurs. Electrical contact is made on both sides of the minimum section by means of wet clay.

Felix Singer[1] refers to the fairly common use of plates with plane parallel faces held between disk or sphere electrodes and generally immersed in oil to prevent arc-over. He also mentions the factors by which the puncture voltage is influenced, some of these being thickness of specimen, the area of the electrode (the greater the diameter the lower the puncture value), the shape of the electrode, the effect of the duration of time to consummate the breakdown (usually the longer the duration the lower the value), the kind of current (direct or alternating), the frequency, and other factors.

The main object in the use of a large plate or a cup is to obtain the puncture through the direct path between the areas on the opposite sides of the same layer of insulating material, and in order to insure this happening the indirect paths between these areas are made long. There are no particular difficulties met with in the actual testing of such specimens. There is some difficulty, however, in the making of both of these types of specimens. For laboratory batches the quantity of material required for a single specimen is large. It is relatively difficult to make and fire uniform plane parallel plates of porcelain.

In the past two years cylindrical porcelain cups made by jiggering have been tested. The dimensions were 6 inches high, 2¾ inches outside diameter, 2 inches inside diameter, with a bottom ¼ inch thick, and a ⅜-inch radius between inside wall and bottom, and no difficulties were encountered in the manufacture. The cup was floated on mercury, and mercury poured into the cup to give the two electrodes. Almost invariably the puncture occurred, not through the relatively thin bottom, but near the much thicker portion between wall and bottom, in spite of the inside curvature. Sometimes the puncture occurred in the wall above the curved portion, having a tortuous path. It was evident that in the jiggering process shearing of the mixture had taken place in the "corner" of the ware, which resulted in an electrically weak structure. Numerous changes were made in the method of procedure and in the dimensions of the test cup, but after a considerable period of experimenting there is no assured success. This situation led to the development of the method herein described, the criterion being the possibility of making a puncture on a simple thick specimen of porcelain, glass, or other insulating material.

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[1] Felix Singer, Die Keramik im Dienste von Industrie und Volkswirtschaft, p. 457 (1923).

Description of "Sealed-in Mercury Electrode" Apparatus

Of several modifications of the apparatus the type here depicted has been the most successful (Fig. 1). Essentially the apparatus consists of two hollow electrode supports, one a glass or metal elbow, the other a straight 6-inch length of glass tubing.[1] The elbow is held in a simple wooden frame. Originally the elbow was made of quartz glass but it has been found that pyrex glass is just as suitable and much less expensive. The metal elbow is made of three parts of ordinary plumbers' cast-iron stock, a length of pipe bent at an angle of 45°, an elbow and a short length whose upper surface has been machined flat. The glass parts have had their rims fire-flashed. Of the various common metals which could be used for the metal elbow it was found that cast-iron has a similar specific resistance to mercury, namely: mercury 94, cast-iron 98, while commercial iron is 9–12, soft steel 16, and hard steel 46.

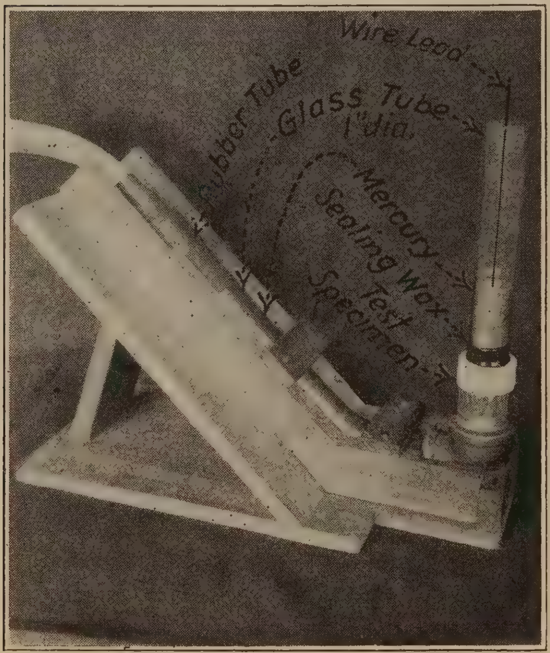

Fig. 1.

Sealing Specimen between Electrode Supports

The specimen to be tested is sealed between the two parts with ordinary red sealing wax. An efficaceous method is to invert the elbow, supporting the framework on a protruding board. A molten mass of wax is brought in contact with the rim of the tube, and by a succession of dips any thickness can be obtained. The specimen is then immediately brought in contact with the wax and after a short period of time the specimen will be held rigidly in place. The upper glass tube is then cemented to the specimen in a similar manner. Mercury is poured into the elbow, and the air entrapped is easily displaced by tipping the apparatus. In the glass elbow it is plainly seen how effective this simple process is in obtaining good contact between the specimen and the mercury. Mercury is also poured into the upright tube. Lead wires put in contact with the two mercury arms of the apparatus complete the circuit. In place of a long glass arm or a long pipe for the inclined electrode, it has been found feasible to use only a short rigid inclined portion with a rubber hose of large diameter attached.

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[1] The inclined tube is either glass or metal. Sealing wax is used underneath the specimen as well as above it.

Puncturing under Oil

For the actual test the whole apparatus is immersed in a bath of oil with the upper ends of the electrode supports protruding. The lead wires are thus maintained quite far apart. The voltage may now be applied and increased until the specimen is punctured, the path of the puncture being confined to the area inside the tubes. The metal elbow has a great advantage over those made of glass or silica glass, for after three or four puncture tests the glass elbows are found to crack below the specimen and near the right-angled bend. Whether this is due to the localized heating or mechanical shock has not been ascertained. The metal elbow after scores of punctures shows no signs of deterioration. The upright glass electrode support is not subject to the cracking.

Preliminary Tests to Determine Limits of Size and Puncture Voltage on Porcelain Specimens

A number of porcelain specimens of different sizes were punctured to determine the critical conditions and the critical dimensions. The specimens were of experimental batches intended for physical tests and are not of the same compositions. Some of the higher values are given in Table I as an indication of the range.

Of the different specimens punctured, the most crucial ones were those 1–1$\frac{1}{8}$ inches in diameter, having an area just large enough to cover the electrode holders. There is no doubt that the glass-sealing wax combination when immersed in oil is a sufficient barrier electrically to prevent arc-over. In air, the apparatus, namely, the metal elbow and glass cylinder with a porcelain specimen sealed between them, withstood 35 to 40 kv. before arc-over occurred around the specimen and through the wax. In this connection there would be great interest

TABLE I
PRELIMINARY TESTS ON PORCELAIN CYLINDERS

Sample No.	Elbow electrode	Specimen Diam. (in.)	Specimen Thickness (in.)	Kv. at breakdown	Volts per mil.
St.	Quartz glass	3	.490	60.8	124
195	" "	$1\frac{1}{8}$	.594	68.0	115
198	" "	$1\frac{1}{8}$	1.125	125.0	(tube broke)
St.	Pyrex glass	1	1.014	128.0	126.5
St.	" "	2	2.037	176.0	(no break) (capacity of transformer)
319 (2)	Cast-iron piping	$1\frac{1}{8}$	1.136	139.2	122.5
" (3)	" "	$1\frac{1}{8}$	1.103	142.4	128.8
" (4)	" "	$1\frac{1}{8}$	1.113	121.6	109.2
" (5)	" "	$1\frac{1}{8}$	1.120	140.8	125.5
St.	" "	3	0.50	64.8	130.0

in determining the most resistant cementing compound by direct comparisons of a large number of them. With a porcelain specimen, $1\frac{1}{8}$ inches in diameter and $1\frac{1}{8}$ inches high, immersed in oil, it is possible to withstand over 142 kv. With a specimen 2 inches in diameter and 2 inches high, over 176 kv. (the capacity of the transformer) were withstood without arc-over.

Comparison of "Sealed-in Mercury Electrode" Method with Sphere and Disk Electrode Methods of Determining Breakdown Voltage

In making this comparison there were two thoughts in mind, the first to determine the value of the "sealed-in mercury electrode" method as a reliable method, and the second to compare it with other standard methods. It was felt that porcelain consisting of a partially fused mixture was not sufficiently homogeneous, not only in composition but also in general structure, for this test. Cast polished plate glass has the advantage that it is made from a homogeneous fluid mass, and in the process of casting is laid down in a uniform layer, with the striae running in sheets parallel to the polished faces. Squares were cut from the same sheet of plate glass having uniform thickness, and were used in the tests, the punctures occurring between the polished faces.

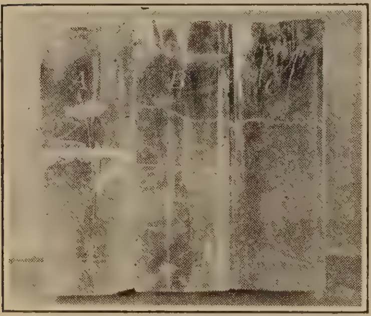

FIG. 2.

Electrodes

The *sealed-in mercury electrode* consisted of a metal elbow tube, $\frac{3}{4}$-inch inside diameter, with a corresponding glass tube. The disk electrodes were also specially made for the test consisting of two brass cylinders, the upper one 2 inches high, 1 inch in diameter, one flat face having the corner rounded to $\frac{1}{8}$-inch radius, and the lower one similar in construction but only 1 inch high. The *sphere electrodes* were two brass spheres, of 1-inch diameter.

Dielectric Strength Test

After the specimen was placed in position between the electrodes the entire outfit was submerged in transformer oil. Alternating voltage of frequency 60 cycles per second was then applied at the rate of 1 kv. per second until puncture occurred.

The detailed results are given in Tables II, III, and IV, and a summary in Table V. Only one specimen, No. 1, was punctured by means of 2-inch disk electrodes, although a number were tried. Specimen No. 1 was a square 3 x 3 inches, 1.068 inches thick and punctured at 84.8 kv., yielding the low value of 79.5 volts per mil. The others arced over and for this reason they were punctured with 1-inch disk elecrodes.

Type of Puncture Path

Visually the path caused by the "sealed-in mercury electrode" method is materially different from the path caused by the disk or sphere electrodes. With disks and spheres the path is a line consisting of what appears to be a series of elongated bubbles in a capillary. In most cases the paths took the shortest distances between planes as in Fig. 2*C*, while in some the paths were curved as in Fig, 2*B*. From the path some small cracks branch off at various depths, but they are only visible when the specimens are viewed through the polished faces.

The specimens punctured by the mercury electrodes can be divided into two classes, those that have punctures similar to the above, and those that have punctures similar to Figs. 2*A* and 3. In these the path consists of a central fused thread from which branch numerous small cracks giving the effect of a spiral. At any depth the cracks branch out in three directions roughly 120° apart.

FIG. 3.

Discussion and Conclusions Based on Results

From the data obtained for plate glass it is evident that the new method of "sealed-in mercury electrodes" gives for a set of homogeneous samples consistent values in electrical puncture tests. The values are also comparable with those obtained by the standard methods using spheres and disks as electrodes, being however, uniformly higher by about 15% for the same thickness of material. The average percentage deviation between values obtained by the "sealed-in mercury electrode" method is small but higher than the deviation calculated from values obtained by sphere electrodes, the disk electrodes giving a much higher deviation.

TABLE II

"SEALED-IN MERCURY ELECTRODES"—CAST POLISHED PLATE GLASS

Elbow of cast-iron piping ¾-inch inside diameter
Pyrex glass tube ¾-inch inside diameter

Specimen no.	Dimensions, inches		Breakdown kv.	Volts per mil.
	Area	Thickness		
2	3 x 3	1.054	121.6	115.3
3	"	1.053	110.4	105.0
4	"	1.064	114.4	107.5
23	1½ x 1½	1.060	129.6	122.3
27	"	1.067	117.6	110.3
31	"	1.067	110.4	103.7
32	"	1.066	108.8	102.4
Average (7)		1.062	116.1	109.5
% Average Deviation				5.0%
22	1½ x 1½	1.004	110.4	110.0
29	"	1.005	116.8	116.2
30	"	1.008	121.6	120.6
Average (3)		1.006	116.3	115.6
% Average Deviation				3.2%

TABLE III

ONE-INCH SPHERE ELECTRODES—CAST POLISHED PLATE GLASS

Specimen no.	Dimensions, inches		Breakdown kv.	Volts per mil.
	Area	Thickness		
6	3 x 3	1.063	102.4	96.4
11	"	1.053	97.6	92.6
12	"	1.067	100.0	93.8
13	"	1.066	107.2	100.5
14	"	1.063	100.8	94.8
15	"	1.056	96.0	90.8
17	"	1.063	96.0	90.3
18	"	1.057	94.4	89.3
19	"	1.068	100.8	94.4
20	"	1.057	99.2	93.9
Average (10)		1.061	99.4	93.7
% Average Deviation				2.5%

TABLE IV

ONE-INCH DISK ELECTRODES—CAST POLISHED PLATE GLASS

Specimen no.	Dimensions, inches Area	Thickness	Breakdown kv.	Volts per mil.
5	3 x 3	1.053	94.4	89.5
7	"	1.057	105.6	100.0
8	"	1.068	116.8	109.2
10	"	1.066	118.4	111.3
16	"	1.062	83.2	78.4
Average (5)		1.061	103.7	97.7
% Average Deviation				11.3%

Numbers 8 and 10 had to be insulated around the rough edges to prevent arc-over and allow puncture to occur.

TABLE V

SUMMARY—CAST POLISHED PLATE GLASS

Electrodes	No.	Av. thickness inches	Volts per mil.	Per cent average deviation
Sealed-in mercury	3	1.006	115.6	3.2
" " "	7	1.062	109.5	5.0
1″ spheres	10	1.061	93.7	2.5
1″ disks	5	1.061	97.7	11.3

The "sealed-in mercury electrode" method has the advantage that it requires a specimen of relatively small area (or a specimen with fairly short creepage path) to effect a puncture test, giving the opportunity of testing numerous samples and parts of samples of insulating materials not hitherto possible. A little more time is required, however, to make the complete test. There is another advantage in that the specimen required is simple in shape and obviates the complicated specimen which requires more time and care in its manufacture.

Better electrical contact is made between the mercury electrodes and the test specimen than between the metal electrodes and the specimen. With the sealed-in mercury electrodes the oil used in the bath does not intervene between electrode and specimen as is the case with sphere and disk electrodes.

The writer wishes to express his appreciation for the help given in this investigation by the staff of the General Engineering Laboratory.

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, N. Y.

SOME SUCCESSFUL CONE 10 SAGGER BODIES[1]

By E. H. Fritz

ABSTRACT

The various steps taken in the improvement of a cone 10 sagger body are described, which resulted in the development of several successful bodies giving a life as high as eighteen firings. Based on these results, a theory is advanced specifying limits for dry modulus, cone 10 absorption, and total shrinkage of the body, which if met regardless of clays used, will produce results such as were here obtained. Verification of this theory by others is requested.

About six years ago, when an enlargement of our plant was decided upon, we were confronted with the proposition of either enlarging our sagger-making department commensurate with the increase in plant capacity which was about to be made, or increase the life of our saggers to a similar degree, due to the fact that it required the capacity of the sagger-making department to furnish enough saggers for the eight kilns which we then had. The results obtained with our saggers at that time indicated that considerable improvement ought to be possible and we therefore decided to depend upon increased sagger life to take care of the plant enlargement. No exact determination was ever made, but as nearly as we can estimate it, our sagger life at that time was six firings. It is therefore not surprising that we felt that improvement could be made. The work which we have done since then has given results which surpassed all expectations. Some idea of them can be obtained from the fact that we have nineteen kilns today and our sagger-making department not only remains unchanged in size, but is making approximately 20% less saggers now than it did when there were eight kilns. How this was accomplished and the conclusions we arrived at in regard to successful sagger bodies at a cone 10 firing temperature, I believe is of interest to others.

Size of Grog

Work was done on the size of the grog and the outcome showed that the grog should not be finer than 12-mesh, of which approximately 75% should be between 3- and 12-mesh and the remaining 25% between 2- and 3-mesh.

Preparation

The preparation of the sagger body was studied, and it was decided to retain the well-known soaking method of getting it ready for the pug mill. However, the soaks were more carefully prepared; all lumps of clay were broken to a size not larger than a medium size ball mill pebble, and alternating layers of clay and grog were not allowed to be thicker than three inches.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (White Wares Division.)

Thickness of the Sagger Bottoms

The saggers had been made with considerable variation in this respect, some of the bottoms being as thin as one-half inch. The weakness of such a sagger is apparent. This condition was remedied and the bottoms were not allowed to be thinner than 1 inch, and for the larger 17-inch diameter saggers and those which carry a heavy load, they were made 1¼ to 1½ inches thick.

Additional changes of a minor nature were made in the sagger-making operation, but those which I have enumerated are the important ones and serve to illustrate the general improvement which was made in the quality and uniformity of this operation.

Clay Selection

Some changes immediately suggested themselves by the dry and fired structure of the sagger body then in use. In the first place, the saggers were too weak when dry, causing considerable handling loss. After firing, the structure was very open and somewhat crumbly. It was therefore thought that a combination of clays, giving more dry strength and a tighter fired structure would give the desired results. Our sagger body, at that time, was as follows:

	Per cent
Tennessee ball, No. 1[1]	25
New Jersey clay, No. 1[1]	15
Pennsylvania colonial clay	10
Grog	50

We determined the dry modulus from test bars in pounds per square inch, absorption at cone 10, and total linear shrinkage on the wet basis for each of these clays and averaged each property for the body according to the percentage composition. In figuring the average modulus and shrinkage the grog was given a value of zero and averaged with the clays. For the absorption, the grog was, of course, disregarded. To illustrate this, I shall give the detailed figures for this combination.

BODY NO. 1, VALUES OF VARIOUS PROPERTIES

	Tenn. No. 1 25%	N. J. No. 1 15%	Pa. colonial 10%	Grog 50%	Av.
Modulus	100	300	0	0	70
Absorption	14%	12%	19%		14.4%
Shrinkage	20%	13%	9%	0	7.85%

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[1] The numbers given with the clays have no significance and are used only to differentiate from clays used later from the same locality.

The modulus of the Pennsylvania colonial clay was too low to get an accurate reading. It is therefore given as zero, although in combination with other clays, it undoubtedly imparts some strength. The average then is the sum of the fractional parts of each property according to percentage composition of each clay. For the modulus this would be (.25 x 100) plus (.15 x 300) plus (.10 x 0) plus (.50 x 0) = 70. For absorption the properties cover the clays only as follows: (25/50 x 14) + (15/50 x 12) + (19/50 x 9) = 14.4%. In a similar way as for the modulus the average shrinkage was obtained.

Plasticity must of course also be considered, but since there is no satisfactory quantitative determination of this property, it is difficult to obtain any definite value. It is understood, however, that this body, as well as others tried, was sufficiently plastic to give a workable body for machine pressing saggers.

In order to increase the modulus and reduce the absorption, substitutions were made in the clays, and the grog reduced to 40%, resulting in the following body, the table giving the proportions, values of the properties, and the averages.

Body No. 2, Values of Various Properties

	Tenn. ball No. 2 15%	N. J. No. 2 15%	Pa. ball No. 1 15%	Pa. colonial 15%	Grog 40%	Av.
Modulus	282	200	150	0	0	95
Absorption	7%	7%	0	19		8.25%
Shrinkage	13%	19%	20%	9%	0	9.15%

This body with its higher modulus eliminated the handling loss that had been encountered with the dry saggers. The fired structure showed the effects of the tighter firing clays, but there seemed to be a considerable amount of small cracks in it after the initial firing. This was ascribed to the higher shrinkage which was 9.15%, as compared to 7.85% for the previous body. This difference was not considered of much consequence and the new sagger mix was adopted and used for about one year. The results were very much improved, the sagger life determined by means of a sagger inventory at the beginning and end of a given period and considering the number of saggers made and the number of kilns fired during the period, being approximately eleven firings.

Further improvement, however, was thought possible to obtain. The modulus and absorption of this body appeared to be about right, but we were suspicious of the shrinkage due to the cracked structure which I previously described. It was desirable therefore to develop a body with approximately the same modulus and absorption as No. 2, but having a lower shrinkage. To accomplish this it was necessary to find a fairly strong, tight firing clay having low shrinkage. A shaley type of clay, such as is found in Ohio, answered these requirements and it was substituted for the Pennsylvania ball No. 1, because this clay had the highest shrinkage and lowest modulus. The Ohio clay is a hard and strong material, but it responds readily to the action of water and develops fair plasticity. It was, however, ground in a dry pan before putting into the soak, to facilitate the action of the water. The resulting body and its properties are shown in the following table.

Body No. 3, Values of Various Properties

	Tenn. ball No. 2 15%	N. J. No. 2. 15%	Ohio No. 1. 15%	Pa. colonial 15%	Grog 40%	Av.
Modulus	282	200	184	0	0	100
Absorption	7%	7%	3.25%	19%		9.09%
Shrinkage	13%	19%	10%	9%	0	7.65%

It will be noted that the average shrinkage for this body is lower than either of the previous two, and the absorption, while slightly higher than No. 2, is still considerably below No. 1. The fired structure seemed improved by this change with considerably less cracks, and had sufficient tightness to appear strong.

In order to determine the life of the saggers more definitely, a lot of one hundred was made up in one of our standard sizes, and assigned to one kiln, to be used for each firing. They were used in the bungs between the bags in every firing. This gave uniform conditions, and at the same time subjected them to what we believe to be the most severe condition which we have. It is here that the heat and flame action is most intense. While the load is not quite as great as in the center of the kiln where the bungs are higher, we believe that the more severe heat conditions over-balance the load difference.

The size of the sagger used for this and later bodies was 12 inches inside diameter and $5\frac{1}{4}$ inches inside depth. The thickness of the bottom was $1\frac{1}{8}$ inches and the side walls $\frac{3}{4}$ inch. No record was made when a sagger became unfit for further use, but instead it was decided what the life of the sagger body would be when one-half had failed. After 15 firings, 52 saggers remained and this was therefore considered the life.

The results with this body when adopted for regular use agreed with the test result. The saggers were by far the best we had ever had and their longer life more than took care of the additional kilns which by that time had been built.

No further work of any importance was done until about a year ago when the receipt of a considerable number of new sagger clay samples suggested trials of entirely different sagger bodies, but having similar average values for modulus, absorption, and shrinkage, in order to determine whether such values might be taken as a basis for a successful cone 10 sagger body. Each trial was made in exactly the same way for the previous body in order to obtain true comparisons. The several bodies tried and results obtained follow.

Body No. 4, Values of Various Properties

	Ohio No. 2 38%	Penn. No. 2 17%	Grog 45%	Av.
Modulus	190	0	0	72
Absorption	5.04%	14.7%		8.0%
Shrinkage	11%	15%	0	6.71%

The Pennsylvania No. 2 clay used in this body is very similar to Pennsylvania colonial clay, except that it is lower in free silica and has higher shrinkage.

The Ohio No. 2 clay is somewhat similar to the Ohio No. 1 used in body No. 3, except that it is considerably more weathered and as a result has greater plasticity. Its modulus is hardly any higher but I believe it exerts more strength than is indicated by the value given. The average modulus as a result is practically as low as body No. 1 but actually was somewhat better. However, the body is barely strong enough for commercial work and the grog should be 3 to 5% lower to improve this.

It will be noted that the average absorption is 8%, which is the lowest which had been tried up to this time. This resulted in a rather tight sagger and brittleness was expected. However, the sagger life proved to be eighteen firings, which was the best so far obtained.

Body No. 5, Values of Various Properties

	Maryland No. 1 10%	N.J. No. 3 15%	N.J. No. 4 25%	Grog 50%	Av.
Modulus	180	265	81	0	81
Absorption	0.27%	12.4%	15.2%		11.37%
Shrinkage	16%	11%	11%	0	6.0%

This body does away with the shaley type of clay, the Maryland and New Jersey No. 3 being of the ball type, while the New Jersey No. 4 resembles a china clay and is another entirely different clay combination.

The average modulus again is lower than No. 3, due largely to the high proportion of grog, but actually the mix appeared sufficiently strong. Its average absorption is considerably higher which was noticeable in the sagger structure. The life determination resulted in eighteen firings or equal to No. 4.

BODY NO. 6, VALUES OF VARIOUS PROPERTIES

	Tenn. Ball No. 2. 6%	N.J. No. 2 16%	Ohio No. 1 16%	Pa. colonial 16%	Porcelain body 6%	Grog 40%	Av.
Modulus	282	200	184	0	350	0	99
Absorption	7%	7%	3.25%	19%	0		8.51%
Shrinkage	13%	19%	10%	9%	13.5%	0	7.67%

This body is a different combination of the clays used in body No. 3 and in addition a small amount of porcelain body which cannot be used again in the regular process. It represents an effort to use this porcelain body material but maintains practically the same average values as No. 3. It gave a life of fifteen firings, the same as obtained with No. 3.

BODY NO. 7, VALUES OF VARIOUS PROPERTIES

	N.J. No. 5 29%	Ohio No. 1 14%	Pa. colonial 14%	Grog 43%	Av.
Modulus	292	184	0	0	111
Absorption	12.2%	3.25%	19%		11.75%
Shrinkage	12%	10%	9%	0	6.18%

Here we have a partial substitution of the clays used in No. 3 through the use of another New Jersey clay. It gave high dry strength and low shrinkage, but the absorption was the highest tried. The life of this sagger was found to be sixteen firings.

Summary of Data

To facilitate comparisons of the various bodies tried, the following table gives the average modulus, absorption, and shrinkage of each body, together with the sagger life in number of firings.

	Body No. 1	Body No. 2	Body No. 3	Body No. 4	Body No. 5	Body No. 6	Body No. 7
Modulus	70	95	100	72	81	99	111
Absorption	14.4%	8.25%	9.09%	8.0%	11.37%	8.51%	11.75%
Shrinkage	7.85%	9.15%	7.65%	6.71%	6.0%	7.67%	6.18%
Life	6	11	15	18	18	15	16

Considering the bodies which gave the best results, Nos. 4 and 5, it is noted that the absorption varies from 8.0 to 11.37% and the shrinkage from 6.0 to 6.71%. It will be quickly seen that none of the remaining bodies come within these limits for both properties. In No. 1 the absorption and shrinkage are higher, the absorption considerably so, and the life is only one-third as long. In No. 2, the absorption is within the limits, but the shrinkage is higher and the life is approximately 60% as long. In No. 3 the absorption is again satisfactory, but while the shrinkage is less than No. 2, it is still slightly higher than the upper limit, and the life is 83% of Nos. 4 and 5. Number

6 classifies the same as No. 3 and the life remains the same. Number 7 shows satisfactory shrinkage, but slightly higher absorption, and the life is slightly lower.

Conclusion

No bodies were tried having lower absorption and shrinkage than the limits of Nos. 4 and 5. As far as absorption is concerned, I believe that lower than 8% would be detrimental, because 8% absorbtion gives a very tight sagger, and lower than that would introduce brittleness and heat strains and lower the heat conductivity. It appears reasonable, however, that a lower shrinkage may improve the results, and this suggests the use of larger proportions of grog and an organic binder to maintain sufficient modulus. The modulus of the bodies tried was satisfactory when above eighty and this value is therefore considered a minimum for satisfactory dry strength. The idea of lower average shrinkage from the use of more grog as well as from new combinations of clays will be tried in the near future.

On the basis of results obtained so far, I would like to advance the theory that a successful cone 10 sagger body must have a dry modulus of not less than 80 pounds per square inch, an absorption at cone 10 of not less than 8%, nor more than 11½%, and a shrinkage of not more than 7%, regardless of what clays are used, assuming that sufficient plasticity is provided, the grog sized to the best advantage, and the body carefully prepared.

Westinghouse High Voltage Insulator Company
Derry, Pa.

TANK BLOCK CORROSION BY SHELVING[1]

By F. C. Flint and A. R. Payne

ABSTRACT

Photographs are given showing a number of glass tanks which indicate that part of the rapid eating of tank block is due to upward solution from cracks in the block wall. This upward solution is due to the higher specific gravity of the glass after dissolving tank block material. Experiments made by adding clay to glass, melted in small pots and analyzing show this. The density is also taken of glass adjacent to the tank wall.

The method of corrosion of tank block has been the subject of a good deal of study and observation. Very often an individual investigator will come to a certain conclusion and stress it so strongly that the implication is left that it is the only method by which the block dissolves. Actually, there are probably a number of factors involved in the solution of the tank block in the glass, no one of which greatly predominates over the others.

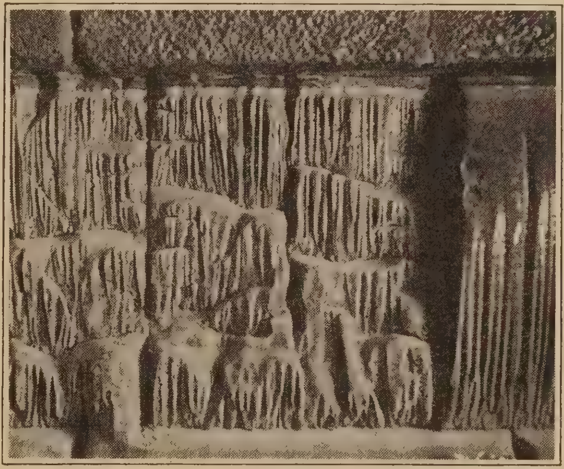

Fig. 1.

The ideas given below and the photographs to support them are given entirely with the thought that this cause of corrosion is only one of many in any given tank of average bottle glass and contributes only its share.

Enough tanks have been examined to indicate that a very large percentage of them corroded, at least partially, in the manner described. This manner of corrosion is by the formation of fine cracks on the inside surface extending gradually into the block, often not reaching the outside surface, the block going into solution at the line where the crack starts, at the inside wall. The block goes into solution quite rapidly along this narrow zone and solution is predominantly upward from the crack, leaving a shelf at the bottom. This is shown by the photographs in which most of the corrosion indicated is upward.

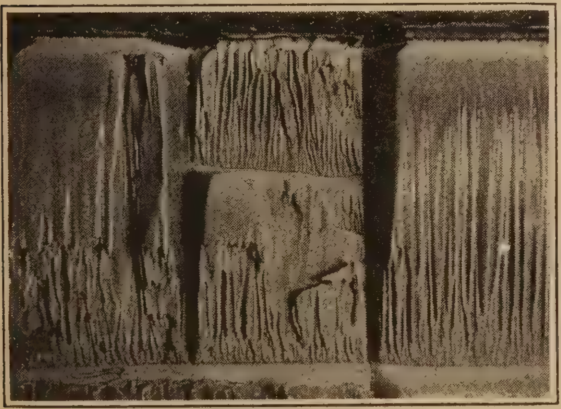

Fig. 2.

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[1] Received July 8, 1926.

Figure 1 shows two 12 x 24 x 30 blocks badly shelved, with a good block to the right. The good block was eaten out from the bottom along the horizontal crack between the courses, but after four and one-half months was not bad, being about ten inches thick near the top. The other blocks are badly shelved, and above each shelf the blocks are eroded very much as the walls of a natural canyon give way by steps. These blocks are only a few inches thick near the top. Corrosion at the bottom seems to have been normal and would have proceeded as on the good blocks, had not the shelving hastened matters by working from beneath at a great number of places.

Figure 2 shows another comparison between cracked and sound block. As usual the sound block are nearly full thickness near the top, but in the cracked block a horizontal shelf cleaned out the top half of the poorest block and the other cracks are gradually eating up from below. The block to the extreme left is cracked vertically. This does not seem to be as bad as a horizontal crack; it does not go so deep.

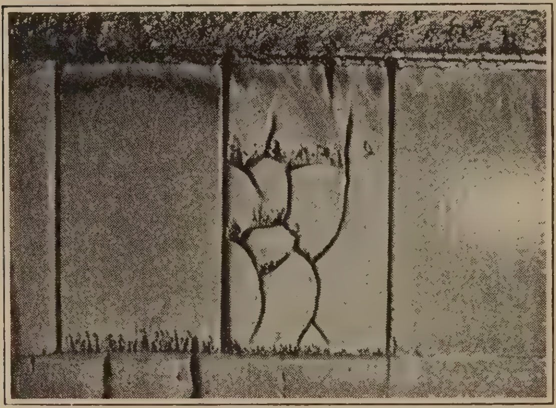

FIG. 3.

Figure 3 is taken from the refining chamber just over the flow hole in the bridge. The top course flux block directly over the flow shows where the hot glass has come up from underneath and corroded the bottom of the block at "A." The bottom course shows deeper cutting. The block to the right being a little distant from the flow is not subjected to the hot glass and is in very much better condition at "B." This is a very good example of the effect of increased temperature on the rate of corrosion of the tank block.

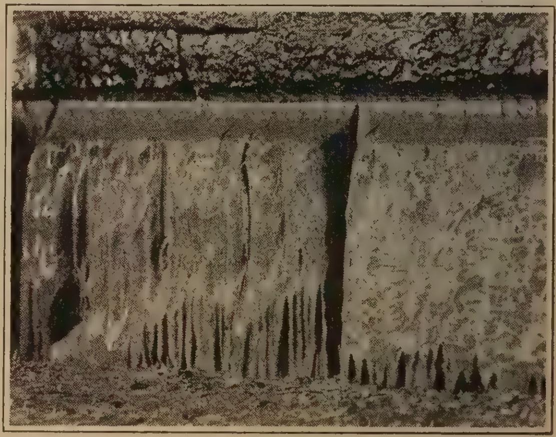

FIG. 4.

The block which is subject to the most wear at the bottom being directly over the flow hole, was in good shape and not cracked and showed little evidence of being attacked by the glass, except at the bottom where the horizontal shelf at the joint started corrosion. The block next to it, however, though not under quite such severe temperature conditions, was very much worse off.

The cracks, looking very much like mud cracks, had sunk in an inch deep where they were off the horizontal and several inches deep where they were horizontal. Also, when horizontal, corrosion had immediately started upward with the customary formation of stalactites and folds. The reason this is not as far advanced as the one previously shown is because the lower temperature has prevented this from going so far in the time used.

Figures 4 and 5 are shown to indicate the effect of shelving and cracks on supposedly similar block of different thickness in a small furnace. Figure 4 is a 12-inch block in a small tank. The one to the left is very slightly shelved, but the crack apparently did not go in very far. The one to the right was in exceptionally good shape so far as cracks were concerned, with the result that very little corrosion occurred. These block started 12 inches thick and were approximately 8 inches thick at the end of the fire.

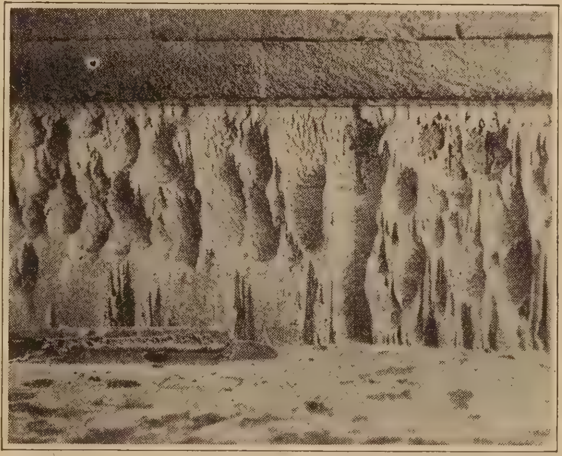

Fig. 5.

In Fig. 5 on the opposite wall of the same furnace, block 8 inches thick were put in to try out the value of an 8-inch block. The experiment was indicative of nothing so far as a comparison between the two thicknesses was concerned because these block were very badly cracked, with the result that they corroded, due to cracks becoming in some places so thin that the water box put on to patch with, could be seen through. It may possibly be that an 8-inch block cracks easier than a 12-inch one, though such is not generally conceded to be the case. It rather looks as if something about the manufacture in these 8-inch block was different from that in the 12-inch which caused them to crack, or it may be that 8-inch block are more susceptible to wind cooling on the outside than 12-inch block, and this caused them to crack.

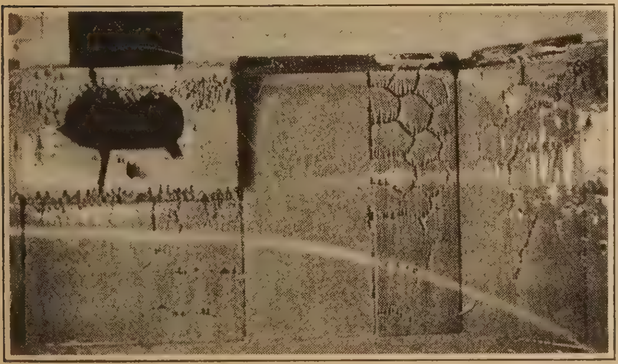

Fig. 6.

Figure 6 is taken from the right front corner of the working end of a large tank. The block in the center is exceptionally good, that next to it badly cracked. Approximately one-third of the block in the refining chamber of this tank were in good shape; the rest of them showed signs of cracking. Here the temperature being only about 2350°F the glass attack was not so rapid as in the melting chamber with a temperature of 2600°F or above.

The upward eating at the crack is again evident. This is also noticed in the skimmer block to the left, the bottom of the skimmer hole being very little touched, the top being eaten three or four inches. These block were made the full 42-inch depth of the tank and so were supposed to get rid of the horizontal joint between the first and second courses. This is true of the good block which introduces no joints of its own, but the majority of the block in the tank contributed far more horizontal joints than would be made in laying up the tank. Most of the block showed evidence of more corrosion near the top of the block than the bottom, though the cracks seem distributed all over. This can be seen in the long block to the right of the good one. The corrosion is due to the effect of temperature on the glass and block. The cracks do not seem to depend on this. The majority of the block examined indicated that they are eaten away from below upward, not from the top down. It is quite common to picture the block as eating out as indicated in diagram A, whereas diagram B (Fig. 8) has been found more often to be descriptive, lines 1, 2, 3, and 4 indicating successive stages in the corrosion of a good block.

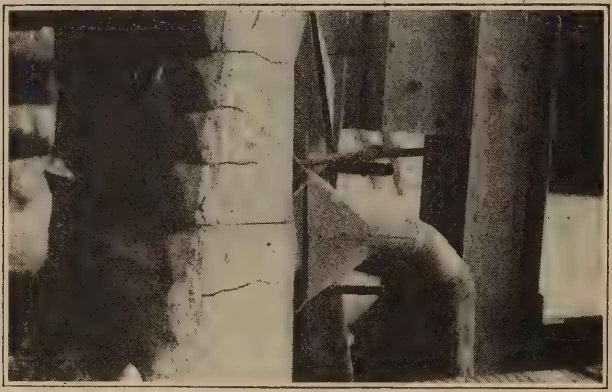

FIG. 7.

These cracks look very much like mud cracks. They may have been started in drying or firing, or in heating up the tank. If in heating up the tank some block seemed able to withstand the temperature change better than others. However, the refining chamber should be heated more uniformly than the melting chamber and in this particular tank nearly three weeks were given to the schedule.

Figure 7 shows the cracks which apparently are causing the shelving. This picture is taken from the inside wall at the rear of the tank at the corner of the dog house. The shelves are shown with the corrosion upward, the shelf extending out nearly to the original inner face of the block except where the shelf below is eaten up to it. The very fine hairline cracks indicated are so small that they had to be penciled in order to be photographed. They were so small that they were barely able to be seen and a thin paper could not be inserted in them. None of them extended to the outside wall of the block; most of them are horizontal, a few vertical ones being shown and one which seemed to start and stop on the interior of the block. Breaking the block would not show this because the block would break along these small hair-like cracks.

The size of the crack does not seem to have a great deal to do with the size of the shelf as can be seen by the horizontal joint between the bottom and top courses. Glass penetration into the crack seems to have been not more than $\frac{1}{64}$ inch at the corner where the shelf stopped and the crack began. This small area was sufficient to extend the corrosion back in the block far more rapidly than the corrosion could attack a smooth face.

This penetration upward may be explained by the increased density of the resulting glass after solution of the clay material. The shelf holds the more saturated, more viscous glass longer, so does not eat away as rapidly, whereas the roof of the crack is quickly exposed to fresh glass, which is farther from equilibrium with the solid phase. This layer of saturated glass in one series of tests was found to be not over $\frac{1}{32}$ inch thick and gave densities as follows:

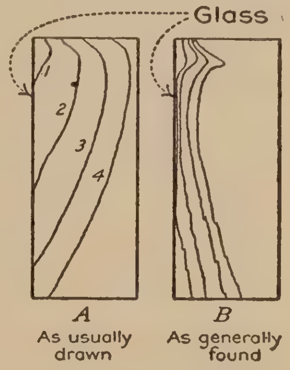

FIG. 8.—Outline sketch of progress of tank block corrosion.

Glass in tank	2.450
Glass near block	2.50 to 2.55
Density of block	2.639

Later this was checked up by melting some glass of a given density and analysis with clay.

GLASS COMPOSITION

		%
Sample of tank glass	SiO_2	74.23
	Al_2O_3 Fe_2O_3	.55
	CaO	4.78
	MgO	3.32
	Alk. (diff.)	17.12
Density		2.4602

		I	II	III
Sample after remelting and introducing clay	SiO_2	71.51	71.62 %	69.74 %
	Al_2O_3 Fe_2O_3	6.74	5.61	6.18
	CaO	4.98	5.91	6.78
	MgO	3.29	3.11	3.32
	Alk (diff.)	13.48	14.35	14.98
Density		2.515	2.493	2.517

HAZEL-ATLAS GLASS CO.
WASHINGTON, PA.

TEMPERATURE OF PYREX AND PORCELAIN IN SUNLIGHT[1]

By J. T. Littleton, Jr. and W. W. Shaver

ABSTRACT

The relative temperatures of Pyrex glass insulators and porcelain insulators in sunlight are determined in three ways. A computation using the radiation and convection heating equations gives a value of 93°C as a maximum surface temperature of porcelain in sunlight, with an assumed shade temperature of 40°C. In a similar way 46.5°C was determined for the Pyrex insulator. Measurements are given of the rise in temperature under natural conditions of Pyrex and porcelain insulators mounted on pins. Temperature measurements were made by means of thermocouples cemented to the surface of the insulators. Extreme conditions were further obtained by means of tin reflectors. Under such conditions the experiments show that the temperature of the porcelain insulator increases on the average about three and one-half times that of the Pyrex glass insulator.

Introduction

The question of the temperature a body may attain when exposed to extreme sun heat such as in the tropics or in the clear air of mountain peaks does not seem to be very definitely established. There are measurements of soil temperatures and measurements of the solar radiation constant but direct observations of maximum temperatures of black bodies in a quiet atmosphere, but subject to free convection, seem to be lacking. Yet these temperatures are of importance when it comes to drawing up specifications for materials subjected to natural temperature changes. Specifications for tests should at least equal the conditions met with in service.

Langley[2] has observed a "hot box" temperature of 113°C. This was obtained by means of a thermometer in a glass-covered box having insulated sides. This would unquestionably be a somewhat higher temperature than would be attained by the surface of a black body of a fairly non-conducting material for the heat loss from the glass cover would be somewhat less than that of the black body since the glass is undoubtedly at a temperature lower than that of the thermometer.

In electrical insulator tests a "hot and cold" test is often specified which demands sudden chilling from boiling water. While it is not claimed that insulators are ever as hot as 100°C in service due to the solar heat it was believed to be worth while attempting to determine just what the maximum temperature of a porcelain insulator might be and also to compare this temperature to that attained by a non-absorbing material such as Pyrex under the same conditions.

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[1] Received June 7, 1926.

[2] Researches on Solar Heat, p. 166, 1884.

Theoretical Computation of Maximum Temperature

The temperature attained by a body can be computed from the known thermal laws. Take first the case of a black disk having very little reflectivity placed horizontally with a corrugated under surface so that convection losses from this surface are negligible. Suppose this disk to be 25 cm. in diameter and 2.5 cm. thick on the average, then let:

T_1 =temperature of upper surface of disk in °A
T_2 =temperature of lower surface of disk in °A
T_3 =temperature of earth and atmosphere in °A
α =conduction of material 2.5 cm. thick per sq. cm. per °C
C=radiation constant for total radiation per sq. cm. in Stefan's equation
K=convection constant for upper surface
E=energy per sq. cm. falling on black body from the sun per sec.

Then neglecting the loss of heat by radiation and convection from the edges we have the following equations:

$$\alpha(T_1-T_2)=C(T_2^4 T_3^4) \qquad (a)$$

$$E=C(T_1^4-T_3^4)+K(T_1-T_3)^{5/4}+\alpha(T_1-T_2) \qquad (b)$$

Where $K(T_1-T_3)^{5/4}$=heat loss by convection from the upper surface per sq. cm. per sec. as found by Montsinger and Cooney.[1]

The solution of these equations is best obtained by trial.

The value of K is 0.00027 and is obtained from Rice's formula.[2]

E is the solar radiation constant and is 0.124 watts per sq. cm.[3]

Assume an air temperature and earth temperature that is T_3 of 40°C.

Determination of T_1 and T_2

Suppose the black disk to be porcelain, then

Specific conductivity for porcelain =.0025 gm. cals. per sec. per sq. cm. per 1°C fall in temp. across 1 cm. thickness

or α=.00411 watts per sq. cm. per 1°C fall in temp. across 2.5 cm. thickness

$c=5.72 \times 10^{-12}$ (to give results in watts per sq. cm.)

E=0.124 watts per sq. cm.

Assume T_3=40°C or 313°A

The solution of these equations gives a

T_1=93°C
T_2=84.3°C

This means that the upper surface of a porcelain insulator might actually be as hot as 93°C in a quiet atmosphere and the under one 84.3°C.

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[1] Montsinger and Cooney, *J. of A.I.E.E.*, Sept., pp. 803–812, 1924.

[2] Rice, "Free Convection of Heat in Gases and Liquids," presented at A.I.E.E. Convention at Philadelphia, Feb. 1924. This value also agrees with the value deduced from Lorentz' formula which was tested out by Langmuir. See *Trans. Amer. Electrochem. Soc.*, **23**, 299–332 (1913).

[3] Smithsonian Tables, value of solar constant for Mount Whitney.

Next consider the case where there is free convection from the lower surface. According to Langmuir,[1] K for the under surface is just one-half K for the upper surface.

Reasoning as before the equations are

$$\alpha\,(T_1-T_2)=C(T_2^4-T_3^4)+=K/2(T_2-T_3)^{5/4} \qquad (c)$$

$$E=C(T_1^4-T_3^4)+K(T_1-T_3)^{5/4}+(T_1-T_2)\alpha \qquad (d)$$

Solving these equations for the case of porcelain we have as before:

$T_1=88.6°\text{C}$ and $T_2=77°\text{C}$

In the case of Pyrex, however, the absorption of the solar radiation is small and will not be in the surface of the material but distributed throughout the body. The conduction factor can almost practically be eliminated.

However, in order to determine just what per cent of the solar heat was absorbed in Pyrex glass, measurements were made in clear air on direct sunlight. For purposes of comparison, samples from two insulator glasses on the market at the present time were also measured. The curve shows the results for Pyrex and the two glasses. It is evident that the absorption of Pyrex is no more than 5%, the loss for zero thickness being reflected light. The data are plotted both on per cent transmission and on a logarithmic scale, the latter being straight lines.

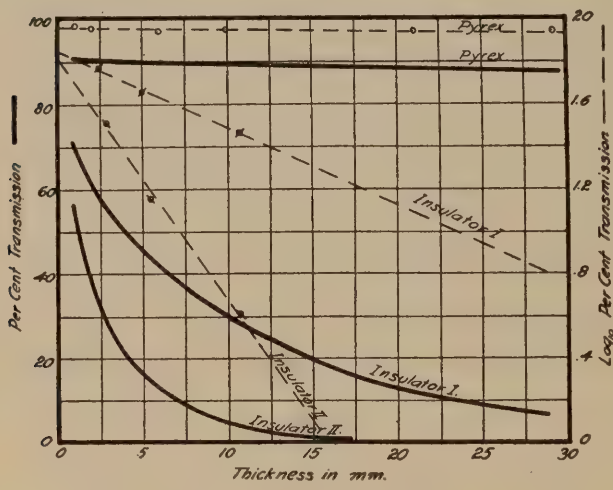

FIG. 1.—Percentage transmission; various insulator glasses.

However, assuming an absorption of 10% in Pyrex, the above equations applied to Pyrex give a temperature of 46.5°C, or a rise in temperature of 6.5°C.

The temperature of porcelain as mentioned above was found to be 88.6°C or a rise of 48.6°C. The ratio of the rise above atmospheric temperature of porcelain to the rise of Pyrex is then 7.5 to 1.

Comparative Measurements of Pyrex and Porcelain Temperatures

Some observations were made on Pyrex and porcelain temperatures in sunlight.

Small light thermocouple wires were cemented on with Dupont cement to the surfaces of porcelain and Pyrex disks. (Dupont cement was found to have almost no absorption.) The disk surfaces were approximately normal to the sun's rays. The table shows the final temperatures obtained. The air was by no means quiet at the time of taking the observations and convection served to keep the values of the temperature down.

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[1] Rice, *loc. cit.*

TABLE I

	Maximum observed temperature rise	
	Front surface	Back surface
Pyrex	2.7°C	2.9°C
Porcelain	20.2	13.4
Insulator glass No. 1	8.1	7.9
Insulator glass No. 2	12.0	11.8
Shade temperature 13.5°C		
Date, May 5		

The porcelain and Pyrex samples were irregular-shaped pieces of similar size and thickness from insulator skirts. The other insulator glasses were small disks approximately 0.4 cm. thick and 2.5 cm. in diameter. It is to be noted that the Pyrex sample is not as hot on the upper surface as on the lower one.

The next test was made May 13 on large pin type insulators approximately of 44,000 volt rating.

The temperature increases were

	Top	Petticoat
Pyrex	0°C	0°C
Porcelain	19.7	1.7

Shade temperature was 22°C; the temperatures were taken after an hour and a half exposure.

Experiments in Intensified Sunlight

In order to determine further just what temperature Pyrex would be when porcelain was at 100°C and what temperature porcelain would be when Pyrex was at 100°C, the following experiments were made at Fort Pierce, Florida. A representative of the Electrical Testing Laboratories of New York City assisted in this experiment and took all the measurements.

Description of Tests The general scheme employed was to mount the insulators to be tested at the focus of a large tinned sheet metal reflector set up in the open and facing the sun, the idea being to get as high, and therefore as extreme, temperatures as possible.

The articles tested were Pyrex glass insulators and porcelain insulators of two general sizes. The large glass insulator and the large porcelain insulator were slightly different, but the small glass insulator and the small porcelain insulator were sufficiently alike to be identical for the purpose of this investigation.

The reflectors were designed by G. S. Fulcher and constructed of ordinary tinned sheet iron and were built up of 32 sectors. The general dimensions are shown in Fig. 2. The reflectors could be rotated in two planes for focussing and could be accurately pointed by means of the shadow cast by the insulator.

The temperatures were measured by means of copper-advance thermocouples of about No. 32 B & S wire cemented to the surface of the insulators with sodium silicate. Any absorption by this cement would tend to increase the temperature of the Pyrex relatively more than that of the porcelain and accordingly it was not deemed necessary to apply a correction for this absorption.

The thermocouples were located at four points on the large insulators, namely: top, right, and left sides and under the petticoat at the bottom of the groove. On the small insulators, the couples were located on each side and on the top.

Temperatures were measured by means of a Leeds and Northrup portable potentiometer type indicator and were observed at frequent intervals, care being taken that the insulators were kept in focus as the direction of the sun's rays shifted. Three sets of observations were made, the first with the large Pyrex and the large porcelain insulators on metal pins, the second with the small Pyrex and small porcelain insulators on wooden pins, and the third with the large insulators used in the first test but on wooden pins instead of metal pins.

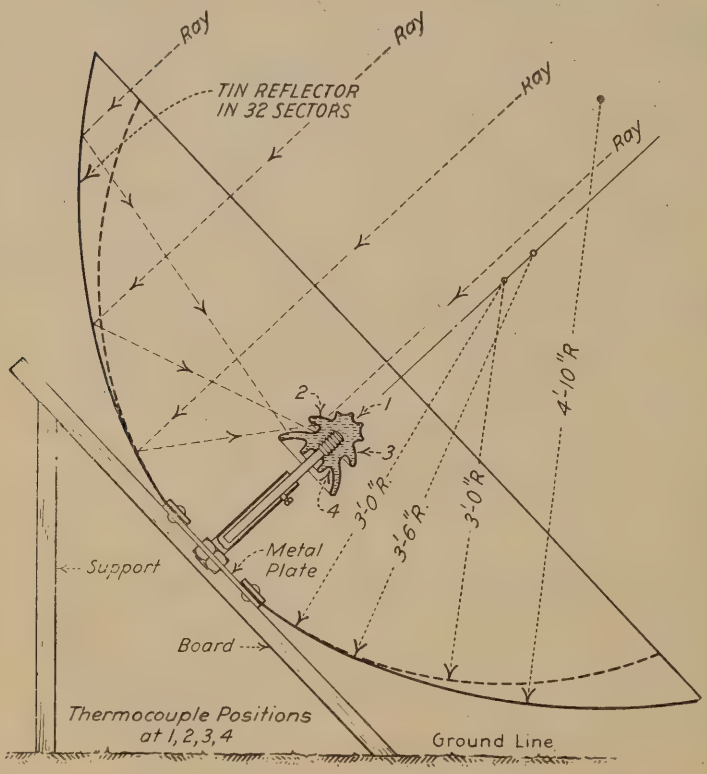

FIG. 2.

Three tests were made with the large insulators on metal pins. In the first and third tests the porcelain insulator was in reflector No. 1 and the Pyrex insulator in reflector No. 2, while in the second test the Pyrex insulator was in reflector No. 1 and the porcelain insulator in reflector No. 2. Two tests were made with the small insulators using wooden pins. The first test was made with the Pyrex insulator in reflector No. 1 and the porcelain insulator in reflector No. 2, and the second test was made with the Pyrex insulator in reflector No. 2 and the porcelain insulator in reflector No. 1. Two tests were made with the large insulators using wooden pins, the tests being made in the same order as were the tests on the small insulators.

The tests were made at Fort Pierce, St. Lucie County, Florida, and at approximately sea level. The atmosphere was approximately dust free but at times showed haze, which quite noticeably affected the results.

After completion of the tests, the insulators and the temperature indicator with the thermocouples were shipped to the Electrical Testing Laboratories where the latter were calibrated.

Observations

The following table summarizes the final results. It shows the maximum temperatures attained by the insulators in the six tests and the mean ratio in each test of the rise of temperature of the porcelain insulator to the rise of temperature of the Pyrex insulator.

	Max. mean temp. °C		Mean ratio of porcelain and Pyrex temp. rise
Test no.	Porcelain	Pyrex	
1. Large insulators on metal pins	151 (No. 2)	78 (No. 1)	3.05
2. “ “ “ “ “	128 (No. 1)	64 (No. 2)	3.6
3. Small “ “ wooden “	136 (No. 2)	66 (No. 1)	3.5
4. “ “ “ “ “	162 (No. 1)	77 (No. 2)	3.15
5. Large “ “ “ “	136 (No. 2)	61 (No. 1)	3.7
6. “ “ “ “ “	135 (No. 1)	55 (No. 2)	4.1
		Mean (Arithmetic)	3.5

The observations taken during the different tests are plotted in Figs. 3, 4, and 5. The temperatures that are plotted are the mean temperatures of all the different thermocouples.

There is not much difference between the mean temperature of the thermocouples and the maximum reading of any one thermocouple in the case of Pyrex insulators but in the case of porcelain these differences were quite high. That is to say, at no time were there any large temperature gradients existing in the Pyrex. This was not the case with porcelain as one

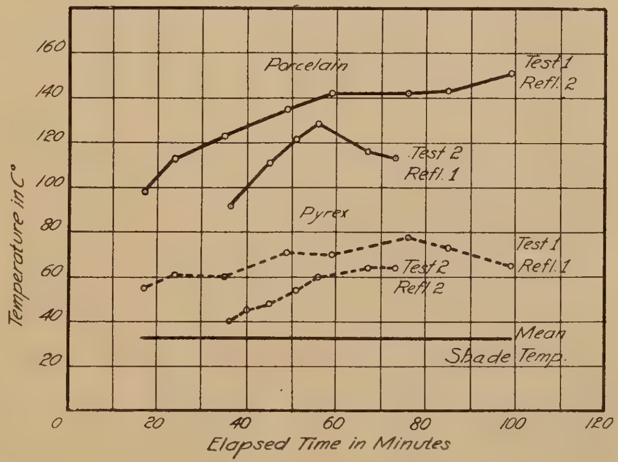

FIG. 3—Temperature curves for large insulators mounted on metal pins.

part of the porcelain would become very much hotter than another portion. The highest temperature observed during the observations at any one point in the porcelain was 185°C.

The simultaneous observations of Pyrex and porcelain taken during all the tests are given in Fig. 6. In this curve the rise of temperature of the porcelain above shade temperature is plotted on one coördinate and the simultaneous rise of the Pyrex is the other coördinate. The curve is drawn through the mean position of the points and has a slope of 3.5. This means that the increase of temperature of the porcelain above atmospheric temperature is 3.5 times the increase of Pyrex. This ratio is somewhat less than the computed ratio. This is probably due to some warming up in the air within the reflector and to some absorption of heat by the thermocouple from the light. In addition the selective reflection of the tin reflector favored the porcelain in all these tests.

The curve given in Fig. 6 or the ratio 3.5 can be used to determine the relative temperature of Pyrex and porcelain under any assumed set of conditions. As an illustration, if atmospheric temperature be assumed to be 40°C (104°F) and the solar conditions such that the porcelain insulator is at 100°C (212°F), that is 60°C (108°F) above atmospheric temperature, the Pyrex insulator will then be approximately 17°C (30.6°F) above atmospheric temperature or at a temperature of 57°C (134.6°F). If conditions are such that the Pyrex insulator is at 100°C, the rise being 60°C, the porcelain rise will be 210°C, the actual temperature being 250°C. On the basis of the computations of possible temperatures these latter temperatures are far above what might be possible under natural conditions.

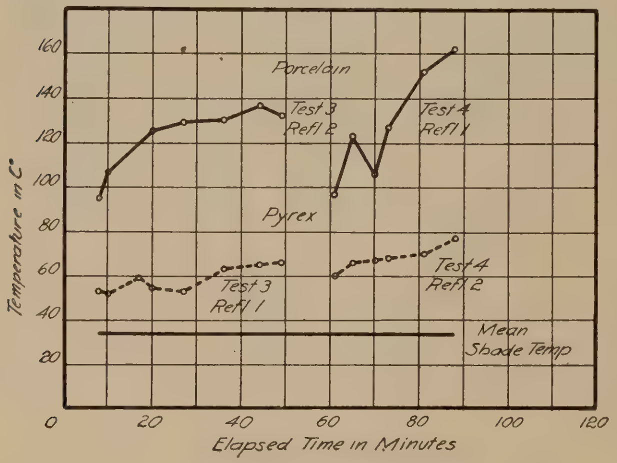

FIG. 4.—Temperature curves for small insulators mounted on wooden pins.

Summary

(1) Computations made using standard radiation and convection equations, give as a possible temperature for a black body when the atmospheric temperature is 40°C (104°F), a temperature of 93°C (199°F). Under these same conditions Pyrex will reach a temperature of 46.5°C (116°F).

(2) Solar heat transmission curves for Pyrex and two commercial insulator glasses have been obtained.

(3) Measurements of the rise of temperature in sunlight of small plates of two insulator glasses and porcelain have been made.

(4) The 44,000 volt porcelain insulator was found to rise in 1½ hours in sunlight 19.7°C (35.5°F). Under the same conditions Pyrex insulators showed no temperature increase whatever above atmospheric temperature.

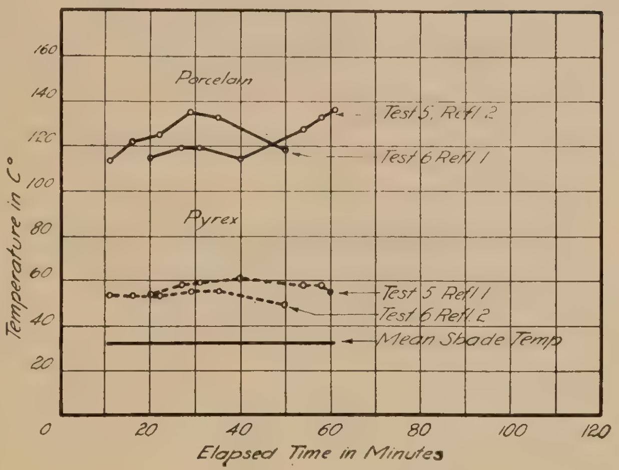

FIG. 5.—Temperature curves for large insulators mounted on wooden pins.

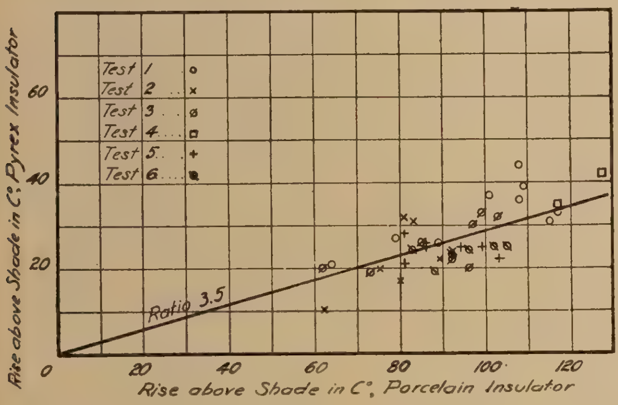

FIG. 6.—Relation between temperature rises of Pyrex and porcelain insulators.

(5) Measurements made at Fort Pierce, Florida, in concentrated sunlight give in a range of temperature up to 160°C, and increase of temperature of porcelain 3.5 times that of Pyrex.

* * *

The authors wish to express at this time their appreciation for the assistance of F. M. Farmer, Chief Engineer of the Electrical Testing Laboratories, and William A. Mahar of the Electrical Testing Laboratories, who assisted in the experiments at Fort Pierce, Florida.

PHYSICAL LABORATORY
CORNING GLASS WORKS
CORNING, N. Y.

A COMPARISON OF THE UNIFORMITY OF STRENGTH AND TEXTURE OF FIRE BRICK MADE BY DIFFERENT PROCESSES[1]

By A. E. R. Westman[2] and W. H. Pfeiffer[3]

ABSTRACT

By assuming that the "deviations from the average" of the strengths and permeabilities of individual bricks of any one brand are governed by the laws of chance, a comparison of the uniformity of strength and texture of a number of brands of brick made by different processes is obtained. Of the brands examined, those made by the stiff-mud process are found to be more uniform in strength and less uniform in structure than those made by the dry-press process. The hand-made bricks show quite a variation in both strength and texture, whereas one brand of brick made by a semi-dry process (English type machine) shows good uniformity in both strength and texture.

I. Introduction

It is the aim of the firebrick manufacturer to produce fire brick which are uniform in strength and texture. In spite of his efforts, however, there is a considerable variation in these properties in the finished bricks. The causes of this variation are many in number and are for the most part fortuitous and beyond the control of the manufacturer. It seems reasonable to assume, therefore, that if the strength or some other property of a sufficiently large number of bricks of one brand were measured, it would be found that the frequencies of the deviations from the average of the individual measurements would have the distribution that would be predicted from the laws of chance. If distribution curves were obtained in this way for several brands of brick made by different processes, a comparison of the shapes of the curves would enable one to decide which manufacturer or method of manufacture produced the most uniform product.

The number of measurements that would be required for the procedure described above make it impracticable. However, if we are willing to assume that the deviations from the average of the strengths and permeabilities of the individual bricks are governed by the laws of chance, it is possible to make a fairly accurate comparison by making measurements on ten or more bricks of each brand.

In connection with an investigation of checker brick for carbureters of water-gas machines, which is being carried on at the University of Illinois,[4] it was necessary to make a large number of measurements

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[1] Received June 8, 1926.

[2] Research Associate, Dept. of Ceramic Eng., Univ. of Ill.

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[4] C. W. Parmelee and A. E. R. Westman, "An Investigation of Checker Brick for Carbureters," *Jour. Amer. Ceram. Soc.*, 9 [5], 290 (1926).

of the transverse strength and permeability of samples of a number of brands of brick. Since the permeability of a fire brick, depending as it does on both the number and diameter of the pores in the brick, is very sensitive to changes in texture, the data made available by this investigation afforded an opportunity for making a comparison of the uniformity of strength and texture which is exhibited by different brands of brick and by bricks made by different processes.

In this paper, the method of analysis which was used in making this comparison and the results which were obtained will be described.

II. Data Available

Transverse Strength The moduli of rupture of fifteen samples of each of fifteen brands of fire brick were available. These had been measured in accordance with the A.S.T.M. method for building brick (C21–20) except that the bricks had been broken on edge instead of flat, as checker brick are ordinarily placed on edge in a carbureter. The transverse strength, method of manufacture, etc., of the fifteen brands are shown in Table I. It will be seen that the fifteen brands included a great variety of fire brick.

Permeability Permeability measurements on ten samples of each of nine brands of brick were available. These had been made by means of a permeameter developed in these laboratories, which will be described in a forthcoming circular of the University of Illinois Engineering Experiment Station.

A schematic diagram of the essential parts of this apparatus is shown in Fig. 1. The brick to be measured is clamped against the felt gasket (*G*) and mercury (*H*) used to seal the sides of the brick. A steady stream of air is forced through the capillary tube (*CT*) of the flowmeter (*F*) and then escapes through the brick. A pressure gage (*PG*) is used to measure the pressure drop across the brick. In making a measurement, the stream of air is adjusted until the pressure gage indicates a pressure drop of 1 cm. water heat 4°C and then the manometer (*M*) of the flowmeter is read at minute intervals until a constant reading is obtained. The flowmeter (*F*) has been calibrated so that it is possible to convert the manometer

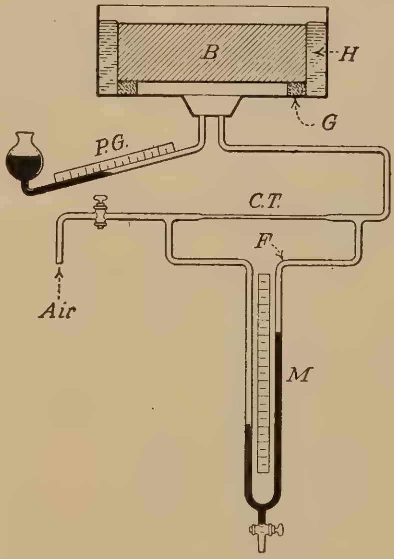

Fig. 1.

readings directly to air flow rates in terms of cc/sec. Thus the rate of air flow through a brick which corresponds to a pressure drop of 1 cm. head of water is obtained. Corrections are applied, when necessary, for the difference between the dimensions of the brick and those of a true standard straight (9 x 4.5 x 2.5 inches) and the value obtained taken as the permeablity of the brick.

III. Analysis of Data

The Per Cent Dispersion of the Average

The problem of making a comparison of the uniformity of strength of the various brands of brick is the same as that of making a comparison of their uniformity of texture or permeability.

Let us consider the case of brand 15, Table I. For this brand we have given the values of the permeabilities of ten samples, as shown in the first column of Table II, in the order in which the measurements were made. The problem resolves itself into a matter of calculating a number from these values which can be used in comparing the uniformity of this brand with that of other brands.

Table I

Data Concerning Brands of Brick Measured

Brand number	Transverse strength (average of 15 samples) lbs. per sq. in.	Permeability (average of ten samples) cc/sec/cm press	Permeability (average of three samples) cc/sec/cm press	Method of manufacture	Raw materials
1	434	4.5		H.M.	Flint and plastic clays
2	426	2.01		D.P.	Cheltenham plastic clay
3	731		300	H.M.	Georgia kaolin
4	843		0.38	H.M.	N. J. plastic clay
5	717	2.9		H.M.	Flint and semi-flint clays
6	1243	0.46		S.M.	Semi-flint clay
7	972		5.7	S.M.	Grog, flint, and plastic clay
8	329	7.6		D.P.	Second grade semi-flint and plastic clays
9	576		6.3	D.P.	Pa. clay
10	1316	1.34		S.M.	Semi-flint clay
11	1245	0.69		S.M.	Plastic clay
12	1478		0.49	S.M.	Flint and semi-flint clays
13	1804		0.64	S.M.	Second grade semi-flint and plastic clays
14	730	5.4		S.M.	Flint and plastic clays
15	911	0.27		S.D.P.	Flint, semi-flint, and plastic clays

H.M.—hand mold
S.M.—stiff mud
D.P.—dry press
S.D.P.—semi-dry press

The theory of errors[1] provides us with a means of calculating the "per cent dispersion of the average" for such a series of measurements. In the case we are considering, if such a quantity has the value "*d*," it indicates that, if the permeabilities of ten more samples were measured and their average permeability were calculated, the new average would be as liable to be within *d*% of the average of the first ten bricks as to be outside of these limits. Such a quantity is sometimes called the "probable per cent error of the mean." It is evident that, if an equal number of samples of two different brands of brick were measured, the relative magnitudes of the values obtained for the per cent dispersions of the average of these two brands would depend on their relative uniformity, provided the laws of chance are applicable. The more uniform brand will, in general, have a smaller per cent dispersion of the average. If, then, we calculate the per cent dispersions of the average for each of the brands of brick under consideration, we shall be able to make a comparison of their uniformities, as the more uniform brands will have a smaller number for this quantity.

Calculation of the Per Cent Dispersion of the Average

The per cent dispersion of the average is calculated as shown in Table II.[1] Column 2 of this table gives the values of the permeabilities arranged in order of magnitude; column 3 gives the deviations of these values from the average (0.261), and column 4 gives the squares of these deviations. If the square root of the sum of the numbers in column 4 is multiplied by 0.6745 and divided by $\sqrt{n(n-1)}$, where n is the number of measurements, the dispersion of the average (0.0071) is obtained. If this is calculated as a percentage of the average (0.261), the per cent dispersion of the average (2.7) is obtained. In actually carrying out these calculations, tables which greatly simplify them can be used.[2]

Chauvenet's Criterion

In a small number of samples, there is apt to be one brick which is so very permeable or impermeable that the inclusion of its value in the calculations would have a very disproportionate effect on the quantities calculated. In order to prevent this, it is conventional procedure to discard a measurement if its deviation from the average is greater than a value calculated by means of Chauvenet's criterion. This value is obtained by multiplying the dispersion or the square root of the sum of the numbers in column 4 by factors which depend on the number of measurements under consideration. These factors are given in practically all texts on theory of measurements. In the example in Table II, the value of the criterion is 0.65 and as the largest deviation is 0.46, none of the measurements was discarded.

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[1] Consult texts on Theory of Measurements.

[2] See "Theory of Measurements," by Palmer, McGraw-Hill, (1912).

TABLE II

SAMPLE CALCULATION (Brand 15, Table I)

Permeability (1) P	Permeability (2) P	Deviation from average (3) v	Squares of deviations from average (4) v^2
0.239	0.217	−0.044	0.001936
0.299	0.221	− 40	1600
0.276	0.234	− 27	729
0.248	0.239	− 22	484
0.307	0.248	− 13	169
0.217	0.276	+ 15	225
0.284	0.284	+ 23	529
0.221	0.288	+ 27	729
0.234	0.299	+ 38	1444
0.288	0.307	+ 46	2116
Average	0.261	Total	0.009961

Chauvenet's criterion $=0.654 \times 0.0998=0.065$

Dispersion of average =

$$0.6745\sqrt{\frac{\Sigma v^2}{n(n-1)}}=0.0071$$

% dispersion of average =

$$\frac{0.0071\times 100}{0.261}=2.72\%$$

TABLE III

UNIFORMITY OF TRANSVERSE STRENGTH

Brand number	% dispersion of average transverse strength (15 samples)	Method of manufacture			
		Semi-dry press	Stiff-mud repress	Dry-press	Hand-mold
*1	5.08				X
*2	4.98			X	
3	4.47				X
4	4.03				X
*5	3.95				X
*6	3.78		X		
7	3.28		X		
*8	2.94			X	
9	2.86			X	
*10	2.81		X		
*11	2.65		X		
12	2.03		X		
13	1.94		X		
*14	1.92		X		
*15	1.76	X			
Average % dispersion		1.76	2.63	3.59	4.38

Uniformity increasing →

IV. Results of the Analysis

From the data which were available, the per cent dispersions of the average transverse strength were calculated for fifteen different brands of brick and are shown in Table III, column 2.[1] The calculations, in the case of each brand, were based on measurements of fifteen bricks whose strengths were within the limits of Chauvenet's criterion. The method of manufacture of each brand is indicated in the table. It is evident that, for the brands considered, the methods of manufacture in order of decreasing uniformity of transverse strength are: semi-dry press (av. 1.76), stiff-mud repress (av. 2.63), dry press (av. 3.59) and hand mold (av. 4.38).

TABLE IV

UNIFORMITY OF PERMEABILITY

		Method of manufacture			
Brand number	% dispersion of average permeability (ten samples)	Semi-dry press	Stiff-mud repress	Dry-press	Hand-mold
6	8.8		X		
5	8.5				X
14	8.3		X		
10	8.0		X		
11	5.9		X		
1	4.8				X
2	3.1			X	
15	2.7	X			
8	2.5			X	
Average % dispersion		2.7	7.8	2.8	6.7

↑ Uniformity increasing

Similar calculations were made using the results of permeability measurements on ten samples of each of the nine brands indicated by an asterisk in Table III. The results of these calculations are shown in Table IV, column 2.[2] As in Table III, the method of manufacture of the different brands is indicated. It is evident that, for the brands considered, the methods of manufacture, when arranged in order of decreasing uniformity of permeability or texture, are: semi-dry press

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[1] The inherent errors in the method of measurement make these values somewhat larger than those that would be obtained with a method that was absolutely exact. If the magnitudes of the inherent errors of the method used are known, corrections can be applied by the method of Shewhart, *Bell System Technical Journal*, 5 [1], 11–26 (1926). In the present case these corrections are small and as only comparative results were wanted, they were omitted.

(av. 2.7), dry press (av. 2.8), hand mold (av. 6.7) and stiff-mud repress (av. 7.8). Thus the order of uniformity of texture is quite different from the order of uniformity of transverse strength, the more permeable bricks being more uniform in texture than the less permeable bricks and less uniform in transverse strength.

V. Summary

An analysis of data on the transverse strength and permeability of a number of brands of fire brick has been made in such a way that it is possible to make a comparison of the relative uniformity of strength and texture of different brands of brick and of bricks made by different processes.

Insofar as the brands examined are representative of fire brick in general, it is shown that:

(1) Different brands of fire brick differ greatly in uniformity of both strength and texture.

(2) Named in order of decreasing uniformity of transverse strength, the methods of manufacture are: semi-dry press, stiff-mud repress, dry press, and hand mold.

(3) Named in order of decreasing uniformity of permeability or texture the methods of manufacture are: semi-dry press, dry press, hand mold, and stiff-mud repress.

(4) As only one brand of brick made by the semi-dry process was examined, its correct position in the series in conclusions (2) and (3) is not as definitely known as that of the other methods of manufacture.

The writers are indebted to C. W. Parmelee, Head of the Department of Ceramic Engineering, for his interest and help.

KERAMEUS OF A WORKER IN GLASS[1]

By W. A. Oldfather

The question of the linguistic correctness of the extension of the word 'ceramic' (from Greek *keramos*) to include the glass industry, has been the subject of two short articles in this *Journal*.[2] The case as there argued, in the almost complete absence of direct testimony, depended largely on inference. It is a pleasure to add to the positive evidence the artist's signature on a glass medallion[3] from early imperial times,[4] now preserved in the Museo Cristiano at Brescia, **BOYNNEPI KEPAMI,** *i.e.*, "Bounneri the potter" (*kerami* being merely late dialectic Egyptian Greek for *kerameus*).[5] In other words, the artist of this remarkable piece of painting on glass calls himself a *kerameus*, showing clearly that in late antiquity, at least, it was perfectly possible to apply a derivative of *keramos* to a worker in glass.

Urbana, Ill.

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[1] Received June, 1926.

[2] *Jour. Amer. Ceram. Soc.*, **3** [7], 526 (1920), especially pp. 537–42; and *Ibid.*, **7** [4], 114–16 (1924).

[3] The most recent and accessible publications of this medallion are those by R. Garrucci, *Vetri Ornati di Figure in Oro Trovati nei Cimiteri dei Cristiani di Roma.* 2nd ed. Rome 1864, pl. XLII, no. 7; Gerspach, *Revue de l'Art Chrêtien*, 1899, p. 50; A. Venturi, *Storia dell' Arte Italiana*, Milan 1901, I, 361, 405; S. Reinach: *Repertoire des Peintures Grecques et Romaines*, Paris, 1922, p. 333, 18; finally, and most elaborately, by F. de Mély, "Le Médaillon de la Croix du Musée Chrêtien de Brescia," *Arethusa* **3**, 1–10 (1926).

[4] The general view has been that it dated from the fifth century after Christ. M. de Mély (apparently with the agreement of Wilhelm Froehner) argues for the third. The rash opinion of R. Garrucci that it is a forgery is amply refuted by the latest authority after detailed study. Wilhelm Froehner (quoted by De Mély, p. 9) thinks it may have been manufactured in Rome in the shop of a Jewish Christian glass worker from Egypt; but this opinion seems a bit speculative.

[5] According to M. E. Crum of the British Museum, quoted by De Mély, p. 6, who adds that it is also the ordinary word for potter in Coptic, derived of course from the Greek. The personal name is probably related to the proper noun "Bouni," in Wessely *Studien*, **10**, p. 156, No. 296, 16, of the seventh or eighth century after Christ, from Egypt, rather than to the "barbarian" names "Bounia," "Bounis," "Bounific . . . . ," of northern Italy and Noricum (*CIL* III 11481 and 11587, and V 7054 and 4169).

EXPLANATION

Explanation of the curves shown in the paper "The Effect of Atmospheric Conditions on the Load Test for Refractories," by L. F. Sheerar, page 279, May, 1926, *Journal of the American Ceramic Society.*

Figures 5 to 13 inclusive should be designated as follows:

FIG. 5.—Effect of oxidizing atmospheres at high temperature on soft-mud specimens containing varying amounts of iron pyrite.

FIG. 6.—Effect of neutral atmosphere at high temperature on soft-mud specimens containing varying amounts of iron pyrite.

FIG. 7.—Effect of reducing atmosphere at high temperature on soft-mud specimens containing varying amounts of iron pyrite.

FIG. 8.—Effect of oxidizing atmosphere at high temperature on stiff-mud specimens containing varying amounts of iron pyrite.

FIG. 9.—Effect of neutral atmosphere at high temperature on stiff mud specimens containing varying amounts of iron pyrite.

FIG. 10.—Effect of reducing atmosphere at high temperature on stiff mud specimens containing varying amounts of iron pyrite.

FIG. 11.—Effect of oxidizing atmosphere at high temperature on dry-press specimens containing varying amounts of iron pyrite.

FIG. 12.—Effect of neutral atmosphere at high temperature of dry-press specimens containing varying amounts of iron pyrite.

FIG. 13.—Effect of reducing atmosphere at high temperature on dry-press specimens containing varying amounts of iron pyrite.

In each figure the upper curve denotes the temperature treatment. The other curves reading from the bottom up, *at the completion of the test* are low iron content, medium iron content and high iron content.

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ORIGINAL PAPERS

SOME OBSERVATIONS OF SURFACE DEPOSITS FORMED IN GLASS FURNACE REGENERATORS[1]

By Herbert Insley

ABSTRACT

Two high alumina refractory brick which had been used in glass furnace regenerators were examined with the petrographic microscope. The deposits formed on the surface of the brick through reaction with the dusts and gases of the furnace atmosphere were found to be composed principally of nephelite, carnegieite, and corundum. Nephelite and carnegieite probably can form only in those parts of glass furnaces where the temperature is considerably lower than that required to melt the glass, but corundum may be formed at melting temperatures.

In a paper[2] by Booze and Flint giving the results of tests to determine the relative resistance of different types of refractory brick in glass tank regnerators to alkaline slags, the authors found, for the particular conditions of the tests, that the brick having the highest alumina content gave the best service. Since the efficiency of the alumina brick as checker brick was somewhat lowered because of the accumulation of deposits on their surfaces, and consequent reduction of air passages, it was thought that a microscopic examination to determine the nature and origin of such deposits might be of importance. The results of microscopic examinations are recorded in this paper. Samples of the used brick were obtained through the kindness of Mr. Booze.

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[1] Published by permission of the Director, U. S. Bureau of Standards, Department of Commerce. Received June 14, 1926.

[2] *Jour. Amer. Ceram. Soc.*, **7**, 594 (1924).

In the investigation reported by Booze and Flint, the specimen brick were installed as an integral part of the upper checkerwork of glass tank regenerators. Temperatures in regenerator No. 1 as measured by an optical pyrometer varied from 1100 to 1200°C (stated as 2000 to 2200°F by the authors) and in regenerator No. 2 from 985°C to 1100°C.[1] The furnace dusts acting on the brick in regenerator No. 1 were high in silica, alumina, alkalis, and lime and the dusts in regenerator No. 2 high in alkalis, lime, and magnesia, and low in silica and alumina.[2]

The specimens examined in this investigation were broken from brick designated by Booze and Flint as of type No. 1 and were reported to contain 34.7% SiO_2 and 58.6% Al_2O_3.

The surface of the brick from regenerator No. 1 was covered with a brown and white deposit, in places curled up into waves, and having the appearance of a dirty coral growth. The interior of the brick was composed of needles of mullite ($3Al_2O_3.2SiO_2$), crystals of corundum (Al_2O_3) and a small amount of glass. The crystals of corundum were observed in masses of friable material and were probably formed by the crystallization of dehydrated diaspor. The white vitreous border zone between the interior of the brick and the surface deposit contained large, well-developed mullite crystals, a small amount of glass, and a very few corundum crystals. The presence of a smaller amount of corundum in this zone than in the interior of the brick was probably the result of the increase in the rate of reaction between the corundum and glass caused by flux penetrating into the brick from the outside. The mullite occurred in large, well-formed crystals while the corundum showed rounded, dissolved borders. Very probably, therefore, the mullite developed at the expense of the corundum and was the stable compound in this zone.

Just outside this narrow vitreous zone, however, corundum seemed to be the stable crystalline phase. Here the corundum developed at the expense of mullite and the glass increased in quantity. A small amount of nephelite ($Na_2O.Al_2O_3.2SiO_2$) was present as skeleton crystals.

The formation of corundum here as well as on clay refractories in other parts of glass tanks is due to the dissociation of mullite. Pure mullite, in the absence of other substances, dissociates into corundum and liquid at 1810°C[3], but such active fluxes as soda and lime undoubtedly lower the dissociation temperature greatly.

In the outer, coral-like deposit the most abundant constituent was nephelite. The indices of refraction of the nephelite, as determined, are: $\omega = 1.538$, $\epsilon = 1.532$. These values agree well with those given by Bowen[1] for pure artificial nephelite ($\omega = 1.537$, $\epsilon = 1.533$) and indicate that the nephelite carries little other material in solid solution. Small corundum crystals are present as inclusions.

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[1] *Loc. cit.*, footnote p. 595.

[2] *Loc. cit.*, p. 597.

[3] Bowen and Greig, *Jour. Amer. Ceram. Soc.*, **7**, 242 (1924).

A schematic representation of the different portions of the brick is given below:

Interior: corundum, mullite, a little glass

Border zone: $\left\{\begin{array}{l}\text{mullite, a little glass, very little corundum}\\ \text{glass, corundum, a little mullite}\\ \text{glass, corundum}\end{array}\right.$

Surface deposit: nephelite, a little corundum

The same type of brick after use in the No. 2 regenerator was very different in appearance because the surface deposit was present as a thin brown skin less than 0.5 mm. in thickness. The interior of this brick was, however, the same as that of the brick in regenerator No. 1 except for a somewhat lesser development of mullite crystals, probably due to the lower temperatures maintained in regenerator No. 2.

The thin outer crust was composed principally of nephelite and carnegieite (the high temperature form of nephelite). The mean index of refraction of the nephelite was $1.540 \pm .002$, which is somewhat higher than that of pure nephelite ($Na_2O.Al_2O_3.2SiO_2$) and probably indicates that other substances were present in solid solution. The carnegieite, in its microcline-like twinning and its extinction angles resembled pure carnegieite ($Na_2O.Al_2O_3.2SiO_2$), but its mean index, $1.533 \pm .005$ was considerably above the mean index as found by Bowen (1.512). The increase in the indices of the carnegieite was probably also caused by solid solution.

The notable difference in the constitution of the crusts on the two samples of brick is that the sample from regenerator No. 1, operated at the higher temperature, contained nephelite only, while the sample from regenerator No. 2, operated at the lower temperature, contained nephelite and carnegieite. That carnegieite, the high temperature form of $Na_2O.Al_2O_3.2SiO_2$, should form only in the regenerator operated at the lower temperature seems unexplainable until it is remembered that substances such as $CaO.Al_2O_3.2SiO_2$ in solid solution with $Na_2O.Al_2O_3.2SiO_3$ alter the nephelite-carnegieite inversion temperature profoundly.[2]

It seems probable, therefore, that the appearance of carnegieite in the lower temperature regenerator only is due to the differences in amount and kind of material in solid solution in $Na_2O.Al_2O_3.2SiO_2$ in the two samples.

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[1] *Amer. Jour. Sci.*, **33**, [4] (1912).

[2] Bowen, *Amer. Jour. Sci.*, **33** [4], 560 (1912).

The occurrence of nephelite and sometimes carnegieite on the surface of refractories above the gas line in the cooler portions of tank furnaces is rather frequent but so far nephelite has not been observed on refractories above the glass line in the melting end of the furnace. The reason for this may be found by considering the course of the attack of the volatilized alkalis and batch dust alkalis on the refractory. The first material formed will be low in alkalis.[1] It will have a softening point which is probably well below melting temperatures in the glass tank. Excess alumina crystallizes from this molten glass as corundum. With temperatures equal to those of the melting end of the furnace, the mobility of the liquid will be great and it will flow away from the surface of the brick carrying corundum crystals with it,[2] and consequently there will be no opportunity for silicates containing high percentages of alkalis to form. If, however, the temperature is in the neighborhood of 1200°C, the viscosity of the silicate liquid will probably be very high and the liquid will remain on the surface of the refractory where it will have an opportunity to combine with more of the alkalis. The resulting product may be nephelite (or carnegieite) which has a melting point of about 1525°C, well above the temperatures in the cooler portions of the tank.

It is evident, therefore, that in the cooler portions of the furnace protective crystalline formations may be built up on the surfaces of refractories with fairly high alumina content (50–75%) while in the hotter portions the same refractories may be corroded away.

Summary

The microscopic examination of two samples of high alumina refractory brick used in glass furnace regenerators shows that the deposits formed on their surfaces are composed principally of nephelite and carnegieite, the low and high temperature forms of $Na_2O.Al_2O_3.2SiO_2$, and corundum. Nephelite and carnegieite probably form only in those parts of glass furnaces where the temperature is considerably lower than that required to melt the glass. These data as well as those reported elsewhere[3] indicate that corundum may be formed in the melting end of the furnace.

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[1] A glass with an approximate composition of $R_2O.Al_2O_3.5SiO_2$ is often found on the surfaces of glass refractories in glass furnaces.

[2] Frozen drops of this liquid containing corundum crystals have been observed hanging from the faces of clay refractories in furnaces torn down for repair.

[3] Insley, *Jour. Amer. Ceram. Soc.*, **7**, 589 (1924).

THE MULLITE CONTENT OF SOME AMERICAN TANK BLOCKS[1]

By Fred S. Thompson and Howard I. Vormelker

ABSTRACT

Samples of the various glass tank blocks manufactured in the United States were analyzed for mullite by the hydrofluoric-acid method.

At present many of the members of the ceramic profession whose main interests are embraced by the glass industry are of the opinion that the presence of mullite in a tank block will lengthen its life by increasing the resistance of the block to corrosion or chemical action of the molten glass and the glass batch. In this study we have made no effort to defend or enlarge upon this theory nor to gainsay it in any manner. We have merely used the best means available for determining the amount of the mineral present in various samples of glass blocks and other materials.

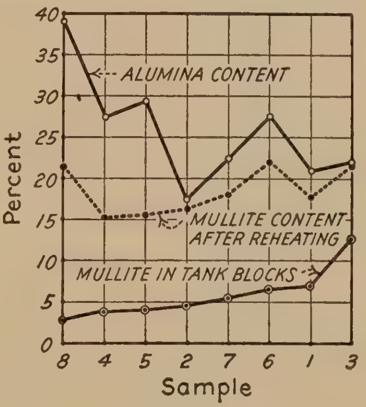

FIG. 1.

The alumina and silica present in a tank block tend to form the mineral mullite when the block is fired to a sufficiently high temperature. This conclusion follows from the thorough study of the problem by Messrs. Bowen and Greig.[2]

W. J. Rees, in his paper on "Alumina Silica Minerals in Glass House Pots and Tank Blocks," gave the following conclusions.[3]

1. That the alumina-silica mineral found in fire clays after firing has the composition $3Al_2O_3\ 2SiO_2$ and is called mullite. This agrees with the work of Bowen and Greig.

2. The proportion of mullite present in fired clay increases with the alumina content of the clay and with the temperature and duration of the heat treatment.

We, therefore, decided to apply the tests as those used by Rees to the same group of tank blocks whose physical and chemical characteristics we described at the Columbus meeting in 1925.[4]

These blocks were obtained from stock and were designated by number. The identification numbers used in this paper are the same as those used in our previous discussion.

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[1] Received August 4, 1926.

[2] N. L. Bowen and J. W. Greig, *Jour. Amer. Ceram. Soc.*, **7** [4], 238–54 (1924).

[3] W. J. Rees, *Jour. Soc. Glass Tech.*, December, 1925.

[4] F. S. Thompson and H. I. Vormelker, "Some Features of Tank Block Comparisons," *Jour. Amer. Ceram. Soc.*, **7** [10], 611–17 (1925).

Our method of determining the mullite content was as follows:

The tank block sample was crushed to a powder and quartered down to about 15 grams. A portion of this representative sample was then ground to an impalpable powder in an agate mortar; one gram of this powder was then added to 20 cc of pure hydrofluoric acid and left for twelve hours at 20°C. The insoluble material was separated by filtration, using platinum vessels. The residue was weighed and analyzed. As the crystalline material is slowly soluble in hydrofluoric acid, the results, hereinafter described, are only approximate; but as a uniform time and temperature of exposure to the acid was adopted, the results are all comparable.

Table I gives all the data bearing on the determination of mullite in the blocks as they came from the kilns of the manufacturers.

TABLE I

Sample Number		1	2	3	4	5	6	7	8
Percentage of sample in residue (mullite)		7.00	4.53	12.78	3.9	4.09	6.54	5.5	2.82
Per cent composition of residue	Al_2O_3	69.1	68.4	71.8	73.8	79.9	69.7	70.1	
	SiO_2	29.4	29.0	26.5	23.3	27.5	26.1	27.9	
	Fe_2O_2	1.0	2.4	1.2	1.9	2.0	4.1	1.6	
Per cent of mullite theoretically possible		29.3	24.8	30.7	38.5	41.2	39.3	31.65	54.3

Effect of Refiring on Mullite Content

About twenty-five grams of each of the original samples were quartered out and fired at 1450°C for twenty-four hours. This treatment produced, in each case a hard vitrified body. The colors varied from brown, in the case of No. 1 to black in the case of No. 6. These vitrified samples were crushed and ground and analyzed as before. Table II shows the results.

TABLE II

Sample Number		1	2	3	4	5	6	7	8
Per cent of sample in residue (mullite)		17.5	16.45	21.78	15.2	15.5	22.01	18.1	21.41
Per cent composition of residue	Al_2O_3	71.9	73.1	72.3	68.2	66.3	68.4	71.1	69.4
	SiO_2	26.1	23.5	26.1	29.4	30.8	27.3	27.1	27.0
	Fe_2O_3	1.2	2.6	1.3	2.1	2.2	4.1	1.7	3.1
Per cent of mullite theoretically possible		29.3	24.8	30.7	38.5	41.2	39.3	31.65	54.3

The general results of the study do not justify any definite conclusions regarding the conditions which produce maximum quantities of mullite. Dr. Rees states that the mullite formed was proportional to the alumina content but our figures and curves show that this assumption does not hold good in ware fired at ordinary kiln temperatures, nor is it true of ware fired at a higher temperature for a period of twenty-four hours.

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WEARING AWAY OF TANK BLOCKS[1]

BY DONALD W. ROSS

ABSTRACT

A statement concerning the manner of the wearing away of tank blocks, factors affecting such wear, and detailed studies of surfaces of used tank blocks.

Statement of the Case

As a rule the wearing away of tank blocks in glass melting furnaces takes place primarily by direct solution. Glass dissolves the exposed block surfaces and forms a clay-bearing glass.[2] This clay-bearing glass is heavier (has a higher specific gravity) than normal glass, and where opportunity offers, it readily sinks. Dissolving of the blocks proceeds in proportion as the clay-bearing glass is removed. However, if this glass is not removed from a given portion of tank block surface, such glass, at and near such surface, becomes saturated with clay and further solution of the surface practically ceases.

Manner of Solution

The clay-bearing glass forming at the tops of blocks tends to flow down over the vertical faces of the blocks and protect them. Wherever there are horizontal joints between the blocks, or defects in the surfaces of the blocks that glass can get into, downward-facing surfaces are present, from which the clay-bearing glass, being relatively heavy, readily settles and flows away and very rapid solution of the blocks results. Such upward eating is characterized by circular holes approximately $\frac{3}{8}$ inch in diameter which are drilled vertically upward, and which apparently greatly accelerate solution of the block.[3] The resulting clay-bearing glass settles on the lower (upward facing) surfaces of such openings, after which reaction practically ceases thereon. This upward eating from horizontal joints and defects apparently results in more eating away of the block than all other eating combined.

Effects of Defects

Of course if a block is not well bonded together, pieces of it may become dislodged and floated away, or if the face of the block shrinks much in use, cracks may open up in it, but in either case, glass gets into the defects and rapid upward eating of the block ensues.

Effect of Tank Depth

As a general rule, solution of blocks is less at the bottom of tanks that are 60 inches deep than in tanks that are 42 inches deep and less in 42-inch tanks than in tanks that are but 30 inches deep. Or in general then, the deeper the horizontal joints are below the surface of the glass, the less will they be eaten.

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[1] Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Atlanta, Ga., Feb., 1926. (Glass Division.) Received May 3, 1926.

[2] S. R. Scholes, "Some Aspects of Tank Block Corrosion," *Glass Industry*, **5** [9], Sept., 1924.

[3] G. V. McCauley, Discussion in "Symposium on Glass Industries Refractories," *Bull. Amer. Ceram. Soc.* **4** [11], 605–608 (1925).

Thus we may expect less eating at the horizontal joint between the bottom and side walls than at horizontal joints in the side walls themselves.

Longer Tank Life Longer tank life then would appear to be favored by the production by tank block manufacturers of blocks having a minimum of shrinkage after being placed in the tank, and containing a minimum of mechanical defects that the glass can get into. It would further appear that the tank block user can himself favor longer tank life by the elimination of horizontal joints between blocks.

This elimination of horizontal joints might even be carried to its logical conclusion and eliminate the horizontal joint between bottom and side walls by having the side wall blocks project down the side of the bottom blocks instead of resting upon them.

Constant care by the glass man during heating up of glass tanks is worthy of his careful consideration, for cracks formed in the blocks through careless heating may be expected to decrease appreciably the life of the tanks.

Technical Aspects

Mechanism of Attack Liquids leaving downward-facing surfaces of solids and passing into less dense mediums, tend to flow to the low points of the solids and leave the solid surfaces at these points.

Clay-bearing glass, being heavier than normal glass, appears to flow along downward-facing surfaces of tank blocks to the low points of such surfaces, and settle from these points through the normal glass. Apparently in this way, the irregularities of the downward-facing surfaces are accentuated so that they eventually assume the stalactite-like appearance which is so characteristic of such surfaces.

The intensity of the interfacial tension at the juncture between solids and liquids (in this case between tank blocks and molten glass) is supposed to vary with the nature of the solid and liquid surfaces.[1] Solution of the block by the glass changes the composition of the glass in proximity to the block, and hence probably also alters the surface tension at the interface between glass and block. It appears possible that under certain conditions this effect may accelerate or retard removal of clay-bearing glass from the block surface.

It even appears possible that the shape of the vertical holes, which is that of a cylinder terminated above by a hemisphere, may exert an effect that tends to accelerate their development upward.

There is frequently, if not always, a thimble-shaped gas bleb entrapped at the upper extremities of these vertical holes. Perhaps the play of interfacial tensions between the gas bleb, the glass surface, and the block surface, may exert an accelerating action on solution of the block.

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[1] R. S. Willows and E. Hatschek, Surface Tension and Surface Energy, pp. 4 and 28.

As has been observed by others, the temperature drop in a twelve-inch tank wall under operating conditions is approximately 180°F per inch from the hot face to the cool outside. If we assume a temperature of 2500°F within the tank at the glass surface there is then a layer at least one inch thick at the hot face of the block that is of such a temperature that further gradual firing of the block takes place in use. In some cases this action probably increases the resistance of the block to solution. This conclusion appears to be borne out by the fact that in recesses or other relatively cool portions of tanks where such secondary firing of the blocks is practically imperceptible and in which nevertheless there has been a normal amount of circulation of glass, the blocks have been found to be badly eaten. On portions of the same blocks that have been exposed to more heat in the tank, the secondary firing of the block has been plainly visible for a thickness of one-half inch to an inch, and relatively little solution of the block has taken place.

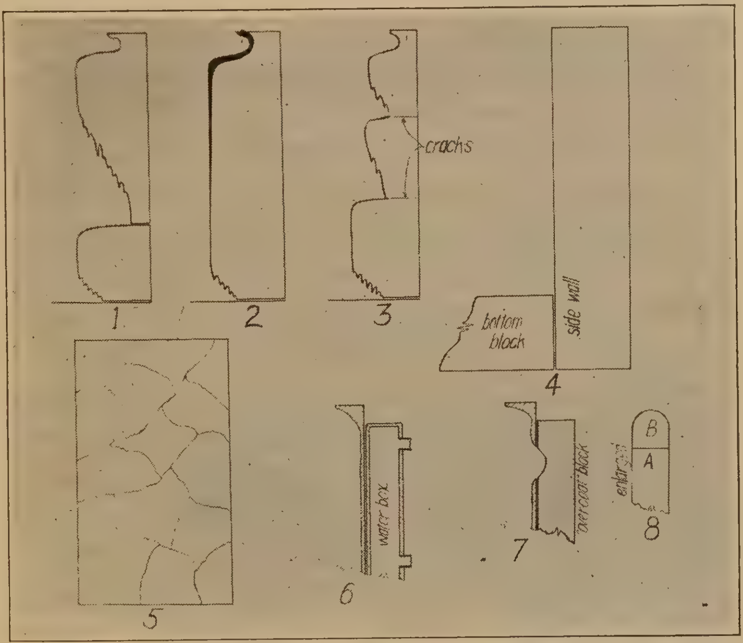

Fig. 1.—Diagrams: (1) characteristic eating of two-course side wall; (2) darkened portion at face illustrates effect of secondary firing during months of use; (3) effects of upward eating from cracks that extend entirely through blocks; (4) method of placing sidewall blocks relatively to bottom blocks to eliminate the horizontal joint at this place; (5) nature of mud-pond cracking in face of blocks that shrink greatly in use; (6) block that during the later part of its life was backed by a water box; (7) block that during the later part of its life was backed by an "overcoat block"; (8) solution hole in a downward-facing surface, A = glass, B = gas cavity; B is lined with a thin layer of glass.

In the case of side-wall blocks that have been in service, and after service were still practically as thick as originally, the effects of secondary firing appear most prominent at the top inner edge of the block and gradually less downward along the inner face of the block, in many cases being practically imperceptible at the bottom of the tank. This appears to be in accordance with the idea that the lower side wall receives less intense heating in use than do the blocks at the metal line. The gradation of this effect is shown graphically in diagram 2, Fig. 1.

Thus, although the effect of secondary firing at times appears to decrease the eating of the block just below the metal line, it probably can not be depended upon to make tanks as a whole invulnerable to solution by molten glass.

Effects of Glass Ingredients Sodium sulphate (as salt water floating on molten glass) and some other sodium compounds appear to be much more active on flux blocks under strongly reducing conditions than under oxidizing conditions, and under such conditions the blocks appear to be destroyed by actual penetration of sodium compounds into the pores of the block, with resulting sloughing away of quantities of the block, instead of a mere dissolving away of the block at its surface. It appears probable that under such reducing conditions the composition of certain soda compounds in glass is altered, and hence possibly also the interfacial tension between glass and block, with the possible result that the soda compounds more readily wet the block and penetrate into it. It may even be possible that this is sometimes accomplished by the formation of minute amounts of free sodium oxide, and that the sodium oxide is the material that actually penetrates into and destroys the block.

In making chemical analyses of difficultly fusible silicates, sodium peroxide is used as the fusion agent, instead of sodium carbonate, on account of its greater efficacy in dissolving such silicates. Hence we may expect that any sodium oxide present in glass-melting tanks at glass-melting temperatures will have an exceedingly active fluxing effect on the tank blocks.

As is commonly known, sodium carbonate is not readily decomposed by heat alone at ordinary glass-melting temperatures. However, it appears probable that at glass-melting temperatures and under rather reducing conditions some of the other sodium compounds used in the manufacture of glass are somewhat dissociated with liberation of small amounts of sodium oxide, which we of course would expect to be very active on tank blocks during the interval until it was converted to sodium carbonate by the furnace atmosphere. In the case of "salt water" it appears probable that sodium sulphate is somewhat dissociated by Co_2 and Co, yielding some sodium sulphide, and if the furnace gases contain much free hydrogen, we might even expect the dissociation to liberate minute quantities of sodium oxide.

Scum Prevention Many manufacturers of tank glass add salt cake to their glass batch, which on rising to the surface of the glass, as "salt water" comes into contact with the reducing furnace atmosphere and dissolves any siliceous matter present at the surface of the glass, and thus prevents the formation of a siliceous scum. This is perhaps an advantageous procedure as the absence of scum permits heat to come into more direct contact with the melting glass batch.

Flux Line However, in the absence of carbon in the batch, it probably does not require much salt cake to result in an excess that floats on the glass and becomes an active agent in the eating of tank blocks at the metal line.

It has been suggested that the scourges of salt water, etc., at the metal line may be somewhat lessened by maintaining the glass line even with the tops of the blocks, so that small amounts of glass run onto the tops of the blocks, the metal line thus acting on an upward facing surface from which the resulting clay-laden glass is not readily removed.

Dissociable Alkali Compounds With reference, then, to the wearing away of surfaces for use against molten glass, it is probably well to consider carefully the chemical nature of the sodium and potassium compounds added to the glass batch, particularly as to the ease with which they are dissociated by heat and furnace atmospheres.

Special or unusual conditions such as large quantities of "salt water" or similar substances on top of the molten glass under reducing conditions, bring about special effects on the blocks. Such conditions as they become better understood, are being rapidly eliminated by glass manufacturers, and being of a local character, do not very generally apply to the dissolving away of tank blocks.

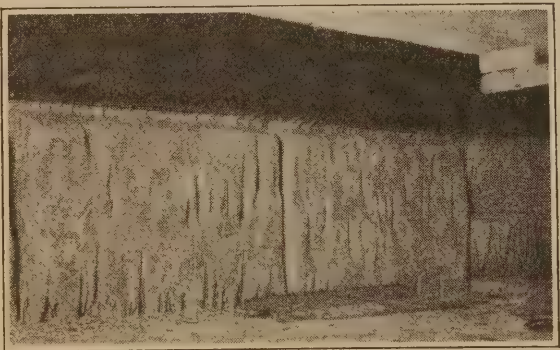

FIG. 2.—Side wall of tank in which there were no horizontal joints and no major defects; blocks were still in very good condition when removed from tank. Compare with bridge wall, shown at right, which was same material but contained horizontal joints. In the bridge the blocks were greatly eaten immediately above the horizontal joints; bottle glass tank that yielded good service and was operated at rather high duty.

Details of Studies of Used Flux Blocks

The features of solution at horizontal joints and defects as described in this paper, occur in both the melting and refining ends of tanks, and hence may perhaps be considered as the normal way in which tank blocks dissolve, rather than as being due to the direct scourges of raw glass batch.

Some of the pictures that might be used to illustrate this paper are already in print in the various trade journals that serve the glass industry, as illustrations of an abstract of this paper. Hence to conserve space these are not here reproduced except as they have special bearing on the text.

In Fig. 1, are shown diagrammatically some of the features exemplified in the photographs shown in the other figures. Diagram No. 1 shows a characteristic form of a two-block high side wall from a tank 42 inches deep (see also Figs. 5 and 6). In this case there has been a relatively small amount of upward eating at the bottom (downward-facing surface) of the lower side wall block. On the upper side of this block (upward-facing surface) there has been little solution of the block. However, at the bottom (downward-facing surface) of the upper block there has been so much solution that a goodly portion of this block has been removed, while the upper portion of this block just below the glass line shows very little solution. This portion just below the glass line apparently receives two forms of protection. First, clay laden glass from the extreme top of the block flowing down over this point would tend to protect it, and second, the effects of secondary firing are apparently most highly developed at this point.

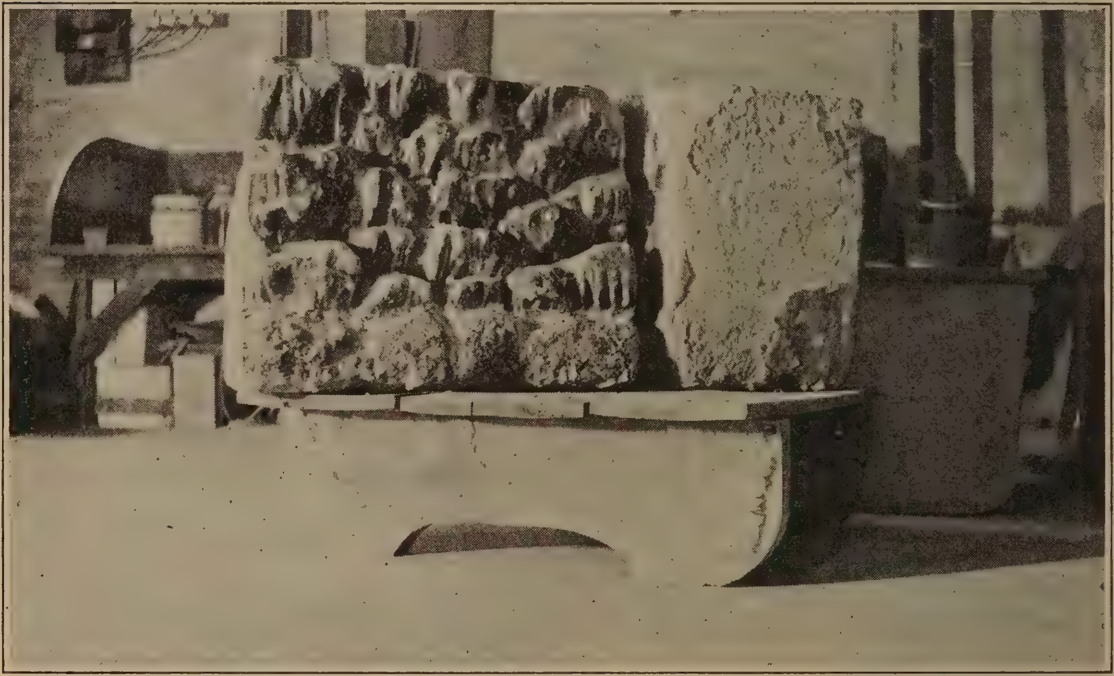

FIG. 3.—These two blocks side by side in service, the face of the right hand block did not crack and showed practically no eating. The face of the left hand block shrunk and cracked badly in use; upward eating started in these defects and practically half the block was dissolved away; side wall blocks, bottle glass tank.

Diagram No. 2 (Fig. 1) shows the gradual gradation of the effects of secondary firing from top to bottom of the side wall, as observed on a block that was the full depth of the tank and was practically full thickness after service. (See also Fig. 9.) The darkened portion represents the part in which secondary firing was observable. Porosity determinations indicated that this effect was practically absent at the bottom of the side wall.

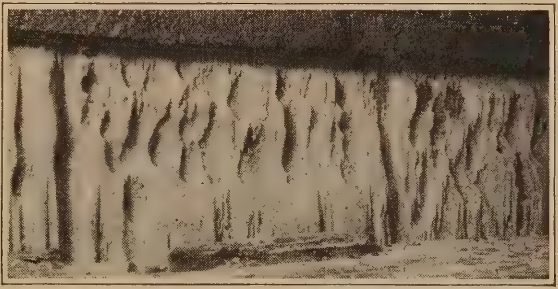

FIG. 4.—As this side wall wore thin from use cracks developed in the exterior of the blocks and extended through to the interior; glass got into these cracks and upward eating ensued. As there was very little downward eating from these cracks, steplike cavities developed in the blocks; bottle glass tank that yielded good service and was operated at rather high duty.

Diagram No. 5 (Fig. 1) shows the nature of cracks that open up in use in the hot face of blocks that contain much residual shrinkage as set in the furnace (see also Fig. 3). This cracking is coincident with the secondary firing of the blocks; that is, as the face burns dense, it shrinks and cracks. In the cases that we have of record to date, such cracks have proved somewhat more detrimental to the blocks than the accompanying secondary firing of the blocks has proved beneficial.

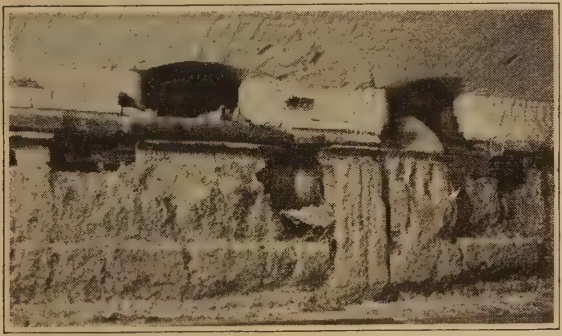

FIG. 5.—Side wall of tank illustrating the use of single-course blocks in comparison with two-course blocks. The single-course blocks were located under the second port from the filling end of the tank and the two-course blocks were ranged on each side of them; bottle glass tank that yielded good service and was operated at rather high duty.

Diagram No. 3 (Fig. 1) shows the manner in which upward eating takes place from cracks that extend entirely through the blocks. Such cracks apparently develop through spalling of the blocks during heating up of the tank or subsequent thereto. Many blocks crack in this manner and as the blocks are worn down somewhat during their later life, the glass gets into such cracks and upward eating ensues (see also Fig. 4).

Diagram No. 6 (Fig. 1) shows a portion of tank wall that has been maintained by a water box or by wind. In such cases the entire surface backed by the water box wears down to a thickness of $\frac{1}{2}$ inch or less and all traces of the nature of previous action on the block disappears. (See also Fig. 5).

Diagram No. 7 (Fig. 1) shows a portion of tank wall that has been maintained by another block being placed behind it. In such cases the glass eats its way right on into the block that is used as backing (see also Fig. 4). Blocks used in this manner are sometimes known as "over-coat blocks."

Diagram No. 8 (Fig. 1) shows a longitudinal section of one of the cylindrical holes terminated by a hemisphere that are so characteristic of the upward eating of tank blocks. The portion *A* is always found full of glass while the portion *B* frequently and possibly always consists of a closed thimble-shaped cavity lined with a very thin skin of glass. The glass surface forming the bottom of this cavity is frequently nearly flat as shown, when taken from the tank in a cold condition. (See also Figs. 7 and 8.)

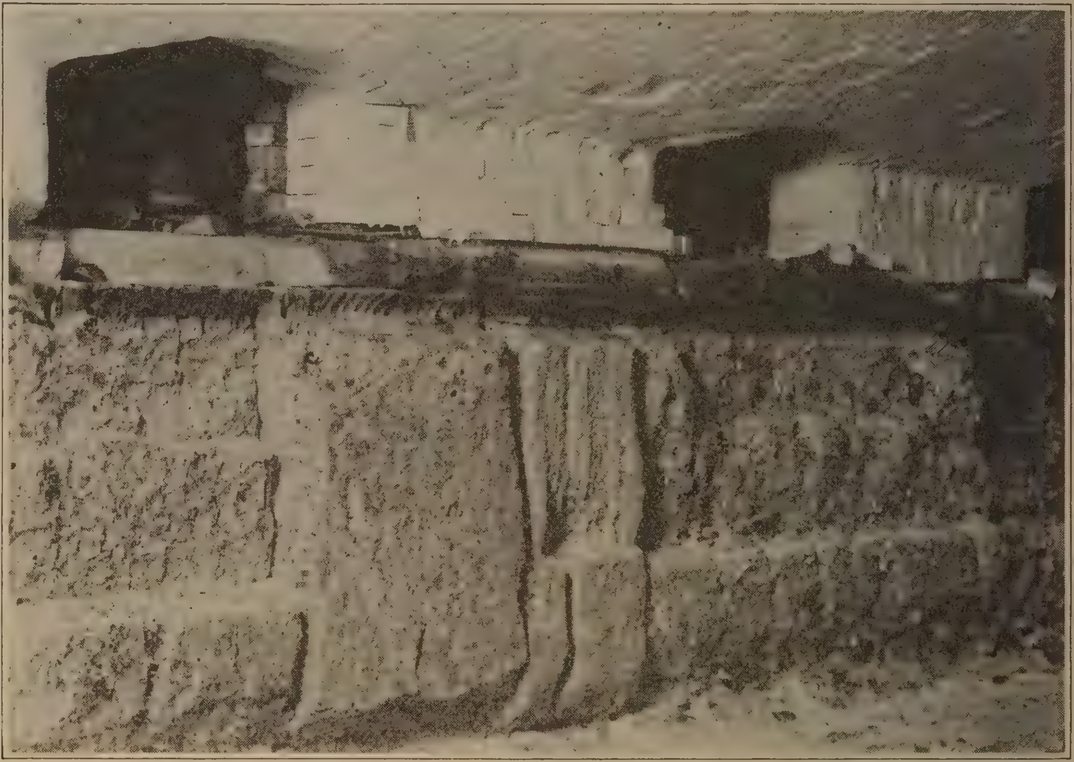

Fig. 6.—Single-course blocks from same tank and same position on opposite side of tank, as the one-course blocks shown in Fig. 5. Comparison of these two figures indicates the similarity of behavior in the two positions in the tank.

Diagram No. 4 (Fig. 1) shows graphically how side wall blocks might be placed relative to the bottom blocks, projecting down over the side of the bottom blocks, if structural conditions permit, so as to eliminate a horizontal joint between bottom and side wall blocks and thus eliminate the type of eating shown at the bottom of the block in diagram 2, Fig. 1.

Photos of Used Flux Blocks As can be seen in Fig. 2, the side wall here shown yielded satisfactory service and at the time the tank was let out might still have been expected to be capable of several months more service. The characteristic stalactite-like form resulting from upward eating is present above the horizontal joints of the bridge shown at the right. The results of glass action at the metal line is shown at the tops of these blocks.

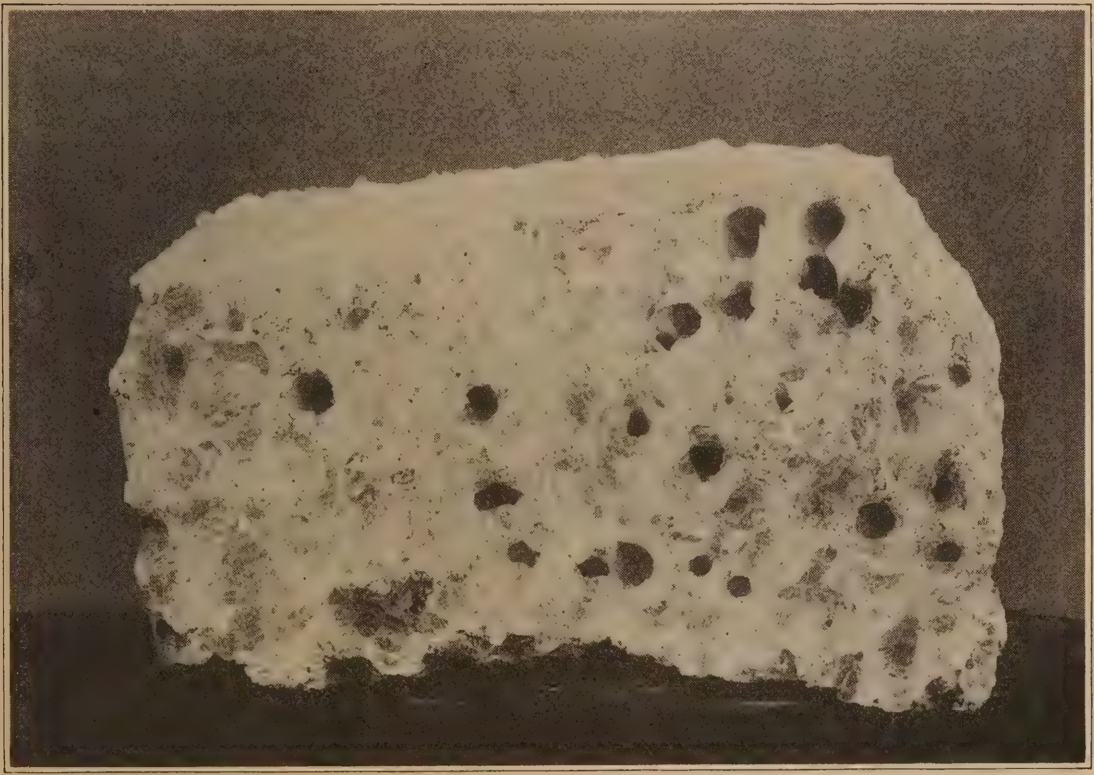

FIG. 7.—Portion of the eaten, downward-facing surface, at the joint between the bottom of the tank and the left hand one-course block shown in Fig. 6. Note the large number of solution holes.

Diagram 5, Fig. 1, indicates how the face of a block such as that shown at the left in Fig. 3 originally cracked. The tops of the knobs shown on the face of this block are practically flat. Apparently the high points of such upward-facing surfaces have been dissolved away, tending to bring the whole upward-facing surface into one horizontal plane. However, the downward-facing surfaces of these knobs have dissolved away in the usual manner, and as seen from Fig. 3, the upward eating has been very effective.

Examination of these two blocks showed clearly that the face of the block at the left had shrunk greatly, while an overall measurement of the face of the block at the right showed that it practically had not shrunk at all.

Diagram 3, Fig. 1, illustrates the type of eating shown in Fig. 4. Examination of these blocks showed that each of the steplike cavities here illustrated extended upward from cracks that, during the latter part of the life of the tank, had been plainly visible on the outside of the blocks. In fact these cracks appeared to be more prominent on the backs of the blocks than on the face, thus indicating that they arose from strain due to thermal expansion rather than from shrinkage of the face of the block. It appears possible that as blocks wear thin and the heat gradient from inside to outside of them becomes very steep, the differences in thermal expansion between face and outside cause the blocks to crack. These are thus a different type of defect than that shown in Fig. 3. The dark areas toward the top of the blocks, near the center of the picture, show where the blocks on becoming thin had been backed up by fire brick and had eaten right on through the original block and into the fire brick. This feature is the same as that shown in diagram 7, Fig. 1. This eating entirely through the flux block is apparently brought about by the insulating action of the firebrick backing.

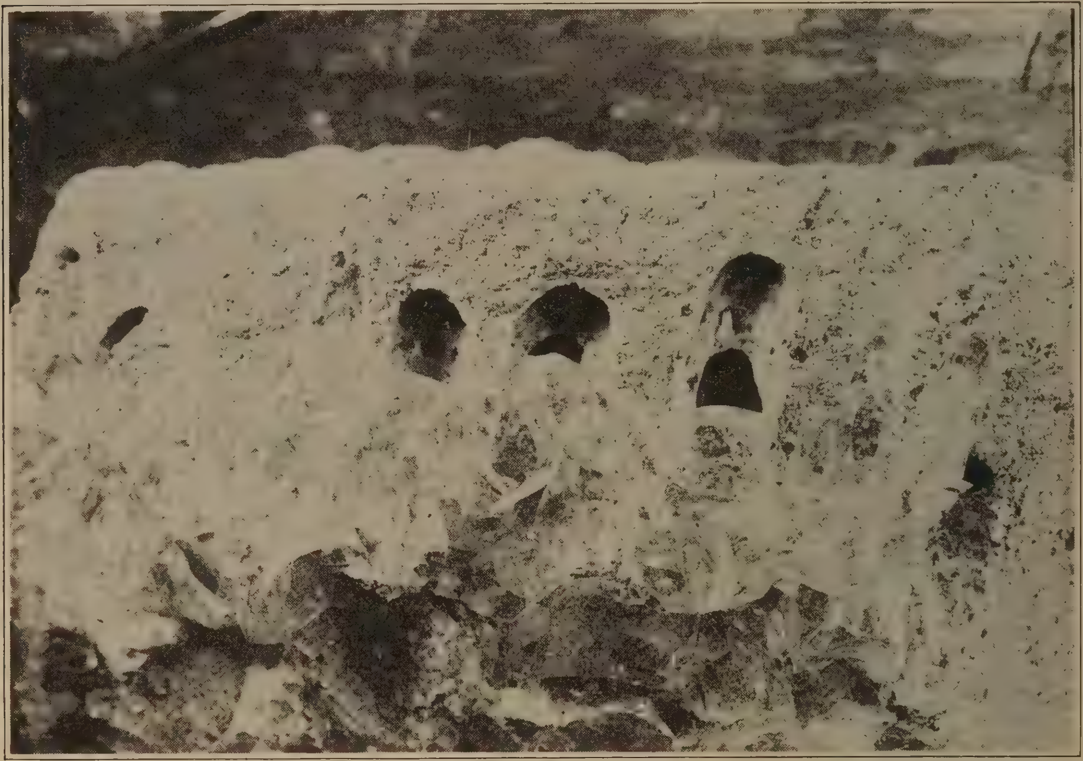

FIG. 8.—Portion of the eaten downward-facing surface, at the joint between the bottom of the tank and the lower side wall block immediately to the left of the one-course blocks of Fig. 5. Note the thimble-like gas pockets at the upper termination of each solution hole.

The upper portions of the upper side wall blocks immediately to the left of the one-course blocks and extending under the third port from the right end of the picture (Fig. 5) were backed by water boxes during the latter part of their service. Note how thin and lacking in detail these portions have become. This is especially apparent in the portion immediatly under the third port. This is an illustration of the feature shown in diagram 6, Fig. 1.

The areas shown in Fig. 6 and in Fig. 5, probably received representative side wall service. Note how closely the form of the two-course blocks approximates that of diagram 1, Fig. 1. In the case of the one-course blocks shown in Figs. 6 and 5, the advantage gained by lack of horizontal joints has apparently resulted in the whole upper portion of these blocks including the metal line, being thicker than the corresponding upper blocks of the two-course portions of the side walls.

The surface shown in Fig. 7 was approximately 6 x 10 inches in area, and faced vertically downward in the tank. The surface shown in this figure has been partly freed from glass and part of the cavities at the upper termination of the solution holes have been broken into. The proximity of these holes to each other is apparent as is also their circular cross-section.

The area shown in Fig. 8 was approximately 3 x 4 inches, and was oriented in the tank as here shown. This piece of block was broken so as to show longitudinal sections of the vertically drilled solution holes in it. This is an illustration of the feature shown in diagram 8, Fig. 1. Such holes develop so close together on downward-facing surfaces that their sides cut into one another as shown in Fig. 8. These thimble-shaped gas pockets at the upper end of such holes have sometimes been overlooked in studies of the wearing away of tank blocks. Hence it has appeared advisable to present here both cross-sectional and longitudinal-sectional views of such pockets. It appears rather probable that the thimble-shaped gas pockets have been present during the operation of the tank. The tank from which Figs. 7 and 8 were obtained was cooled down full of glass. It appears hardly probable that gas was sucked in through the porous block to form these pockets during cooling of the

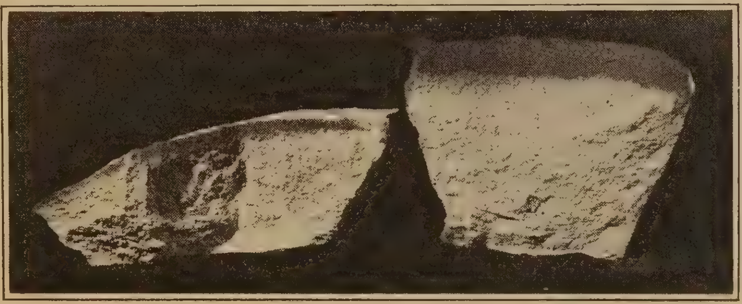

FIG. 9.—Face of side wall block showing effects of secondary firing of blocks in service. Piece at right is from metal line. Piece at left is from lower portion of side wall.

glass, for each of these pockets is lined with a thin skin of glass that appears to be unbroken. Tank blocks as a rule are sufficiently porous that gas can slowly pass through them and yet it appears probable that gas pockets such as those shown in Figs. 7 and 8 persist for considerable lengths of time. Possibly the film of glass lining the interior of these cavities serves to entrap the gas.

Figure 9 is an illustration of diagram 2, Fig. 1. The photographing of the shadings in tank blocks due to different degrees of firing required a somewhat special procedure. The colorings in this case were a bluish color in the region showing secondary firing and a tan color in the adjoining material. A panchromatic plate was used and a yellow ray filter was used over the lens.

The feature illustrated in Fig. 9 is not readily identified in all used tanks for the faces of many blocks are usually considerably eaten. However, it can frequently be identified where blocks occur that show practically no eating from metal line to near the bottom of the tank.

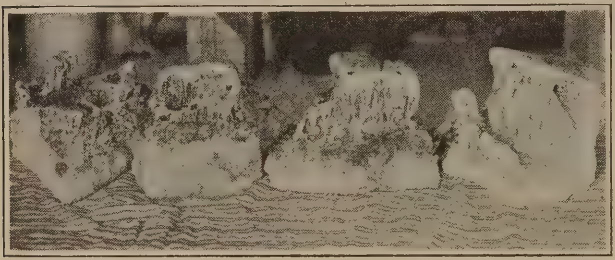

FIG. 10.—Upward-facing surfaces from which the clay-bearing glass was apparently swept as fast as formed, with the result that active dissolving of the surfaces took place.

The pieces photographed showed clearly that although the piece from just below the metal line had received considerable secondary firing to a depth of nearly $\frac{3}{4}$ of an inch, the portion from the lower side wall was apparently unaffected at a depth of over $\frac{3}{16}$ of an inch.

By secondary firing is meant the gradual firing that the blocks received through the glass during months of service, and not the intense surface heating occasioned by bringing the tank to glass melting temperatures before filling it, which latter probably does little more than tend to form cracks in the face of the blocks similar to the type shown in diagram 5, Fig. 1, and which subsequently afford opportunity for upward eating.

The pieces shown in Fig. 10 have been severely eaten in spite of the fact that in service they constituted upward-facing surfaces. These pieces were so located that currents of glass continuously passed over them, and it appears certain that clay-bearing glass was continuously and perhaps forcibly swept away as fast as formed. Examination of these pieces indicated that the progress of the glass downward into the block occurred largely by the glass following defects and that wherever these openings presented any downward-facing surfaces, upward eating became an important factor, thus tending to cut away any material above the lowest level. The plateau-like areas, shown best on the left hand piece, illustrate the fact that projections on an irregular horizontal surface tend to become "penaplaned" off, forming nearly plane horizontal surfaces. The sloping surface on the second piece from the left is evidently where glass got into a fissure, and the little niche in the left hand part of this slope indicates how upward eating has started from a defect therein. The third piece indicates how general the upward-eating effect can be. In this case very minor openings in the body have apparently served as means whereby upward eating could start. Examination of the defect at the right hand side of the right hand piece showed clearly the manner of upward eating from a downward-facing surface of a defect.

The evidence obtained from these materials shown in Fig. 10 appears to be direct substantiation of the conclusions expressed herein concerning solution of vertical wall blocks and of flux blocks in general, by molten glass.

Summary

In summary then, we have set forth, first, that glass tank blocks are worn away largely by solution of downward-facing surfaces, that such eating is largely eliminated by elimination of horizontal joints, and that the deeper any horizontal joint is below the metal line, the less it is eaten. Second, excessively reducing tank atmospheres apparently accelerate solution of the blocks at the glass line, this being particularly noticeable in the case if there is an excess of "salt cake" in the batch. Third, detailed examination of used tank blocks appear to substantiate our statements and indicate that thimble-like gas blebs are frequently, if not always, present in the upper extremities of cavities in downward-facing surfaces, at least after the glass is cold.

THE FINDLAY CLAY POT CO.
WASHINGTON, PA.

THE SPALLING OF BRICKS[1]

By F. W. Preston

ABSTRACT

Spalls in spalled bricks are, under the conditions postulated by F. H. Norton, tensile, not shear fractures. The surface of separation bears no simple relation to the isothermal surfaces. In a "semi-infinite" slab, the diffusivity has no influence on the tendency to spall, but does influence the location of the surface of parting.

A very interesting paper by F. H. Norton on the subject of spalling was published by this Society.[2] The behavior of a solid material at rupture is a matter of quite unusual complexity and one that has never been reduced to mathematics. Mr. Norton's attempt shows courage in attacking a very difficult problem, and if any guidance may be attained in showing how refractories may be made more thermally-resistant or enduring, such attempts should be warmly welcomed.

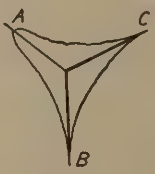

Fig. 1.

The matter is, however, a problem quite other than Mr. Norton has assumed; the mathematical work is incorrect and the underlying physical assumptions are faulty.

The spall fracture of a brick, which usually takes place at a corner, does *not* follow an isothermal surface, nor a surface related in any simple way to the isothermal surfaces. The fissure in a typical case enters *normally to the isothermals*, at right angles to the tension, then bends around sharply, removing the corner, and makes its exits tangentially at other edges. An idealized spall is shown in Fig. 1. It enters the brick normally to the edge at *A* and leaves tangentially at *B* and *C*. An actual example of a typical spall in a silica brick is

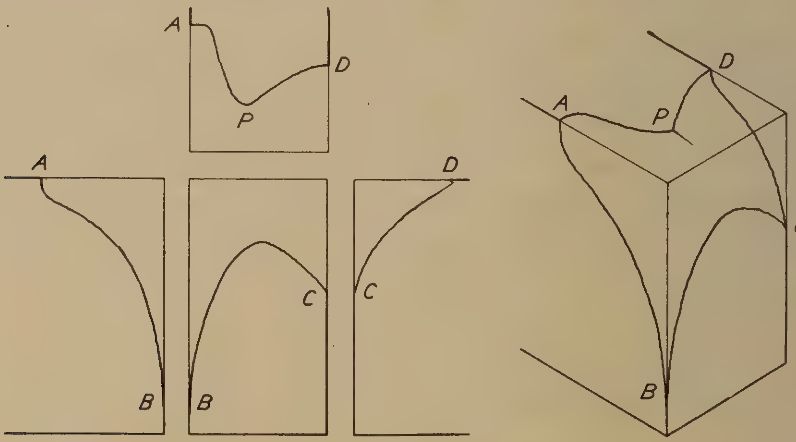

Fig. 2.

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[1] Received April 8, 1926.

[2] Norton, *Jour. Amer. Ceram. Soc.*, **8** [1], 29–39 (1925).

shown in Fig. 2. The primary spall entered at A and ran out toward B; but simultaneously another spall started at D, met the first one at P, and the combined spall broke out nearly tangentially at C and quite tangentially at B. Note that at A and D the fissures entered normally.

The form of these fractures shows that they are tensile, not shear, failures. I have dealt elsewhere[1] with similar fissures in glass and shown that in a multitude of forms these fissures are all tension-failures.

Mr. Norton has preferred a mathematical attack on the problem, and being misled by the supposition that the fissure follows approximately an isothermal surface has elaborated his treatment, not for a corner, but for the plane isothermal parallel to the surface of a semi-infinite solid.[2] The mathematical treatment is however erroneous, for in an infinite solid of this sort, the isothermal planes, which are parallel to the face of the solid, are also surfaces of principal stress, and therefore surfaces of zero shear. There is no shear on any of these planes and Mr. Norton's equation (3) is unfounded.

Before the fissure starts there is no tension across the isothermal surface; the tension is entirely parallel to it. But when the fissure has once entered normally to the face, the stress distribution is radically altered, though the temperature distribution is not. Thus at the very beginning the fissure is connected in a simple way with the temperature distribution—the fissure is at right angles to the isothermals (exactly contrary to Mr. Norton's view that it is parallel to the isothermals)—but after the first instant the fissure travels in a manner related only in a most complex manner to the temperature distribution. It travels in such a manner that at any instant its direction of advance is at right angles to the principal tension; that is to say, the direction of the fissure bears a very simple relation to the stress distribution at the instant, but virtually none whatever to the temperature distribution or to the *original* stress distribution.

It is very important to realize that in the formation of a spall, the spall does not separate from the brick instantaneously and simultaneously at all points. Some parts of the surface of separation form ahead of other parts. The process can be very readily watched in glass specimens.[1]

Before the fissure opens the temperature distribution and the stress distribution are alike perfectly calculable.[3] But when the fissure has once begun, the stress distribution becomes radically different and is beyond mathematical analysis, and the form of the surface of separation cannot be computed. But the advance of the fissure follows the law given above: *viz.*, it proceeds at right angles to the principal tension at the head of the fissure. This really defines the conditions uniquely, but it is interesting to note also the connection between the fissure and the strain-energy content of the brick.

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[1] *Jour. Soc. Glass Tech.*, **10**, September, 1926.

[2] Norton, *loc. cit.*, p. 32.

[3] See for example Adams and Williamson, *Jour. Franklin Inst.*, **19**, 835–70 (1920).

The temperature-gradient soon after quenching is substantially as shown in Fig. 3. Over the greater part of the thickness the temperature is sensibly unchanged, and $d\theta/dx$ is zero. Near the surface, $d\theta/dx$ is large and sensibly constant. The two parts are joined by a sharp-radiused curve. This part is the region where the tension of the surface layers gives place to the compression of the central layers.

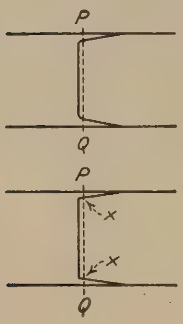

FIG. 3.

Instead of troubling about the theoretical form of the curve, let us replace it by a sensibly equivalent one as shown in the next figure, where the sharp-radiused part is suppressed. The stress curve is similar to the temperature curve. Let PQ be the line of mean temperature (averaged throughout the thickness): then it is also the line of zero stress. When the "curve" passes to the left of this we have compression. When it is to the right, we have tension.

The spall will tend to form through the point x, separating the tension area from the compression area, for by so doing it *liberates the maximum amount of strain energy.* Or better expressed: the energy needed to form a fracture is built up on quenching in the form of strain energy; at a given critical instant enough strain energy is available to split the brick, provided that the fissure forms at x, and so releases practically all the strain energy. The condition of affairs is then as in Fig. 4. The compressed central piece C is relieved of its compression (but if C is thick not much energy is available from this source). The spalls A and B curl up, each fiber thereof achieving its natural length (the length appropriate to its particular temperature). Most of the strain energy comes from these pieces.

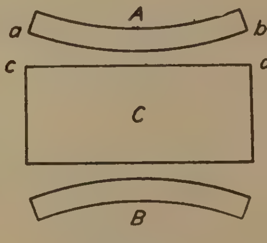

FIG. 4.

Note that as the face AB of the spall is at the same temperature as the face CD of the brick, these faces will be of equal length even after separation, and both will be sensibly equal to the length before separation (for the compression in C is small, owing to the great thickness, and it does not expand much to lose its compression).

Now without letting any further change of temperature take place, let us try to put the spalls back by main force. Then it is evident that our principal need is a supply of tractions acting normally to the face *CD*, like a number of threads of cotton, to unbend the spall.

The curvature of the spall is given by $\frac{1}{R}=\alpha\frac{d\theta}{dx}$ where α is the coefficient of expansion and $d\theta/dx$ is the (sensibly constant) temperature gradient throughout the thickness of the spall.

To flatten the spall out again by mechanical effort requires a bending moment that can be readily calculated from ordinary beam-philosophy. Let I be the sectional moment of inertia of the spall, M the bending needed, and E Young's Modulus, then $\frac{1}{R}=\frac{M}{EI}$.

Equating this to the thermal curvature gives $M/I=E.\alpha.\ d\theta/dx$.

This *BM* will flatten the spall, but it will now be a little too short, and we shall have to add a direct tension to stretch it a trifle. The horizontal stress, parallel to the face introduced by the bending moment M is readily calculated, and adding thereto the stress needed to effect the final stretching of the flattened spall we get for the stress in the extreme fibers $f=E\alpha(\theta_2-\theta_1)$, where θ_2 is the temperature of the brick before quenching and θ_1 the temperature of the quenching water.

If the "severity of quenching" $(\theta_2-\theta_1)$ is too high, or if the coefficient of expansion α is too high, or if Young's Modulus E is too high, the stress, f, becomes very great and if the tensile strength of the brick is low, or if flaws or fissures are already present, the brick is likely to spall. Note that in this result the stress developed is *independent of the diffusivity*. Such a result is of course inevitable, for we have supposed our solid to be infinitely thick compared with the region where $d\theta/dx$ is large enough to be measurable. It follows that the compression layers, being very numerous, are only infinitesimally compressed, so that the whole stretch is concentrated on the surface layers, where, at the extreme surface, it amounts to $\alpha(\theta_2-\theta_1)$.

This stretch is independent of the time and remains constant until the central layers of the brick lose their heat.

Thus the tension developed in the most highly stretched layers is proportional simply to Young's Modulus, the coefficient of expansion, and the "severity of quenching."

It is readily seen, however, that the diffusivity becomes a matter of consequence when the slab is thin, since it settles the maximum value of $\theta_2-\theta_1$ that can obtain after any perceptible length of time, but more on this point later.

Theoretically a brick should either spall at the first quenching or else stand an indefinite number of quenchings of the same severity.

Mr. Norton observes something to that effect.[1] The proper way to determine the spalling properties of a brick would seem to be to determine the severity $(\theta_2 - \theta_1)$ which will *always* spall the brick at the first quenching.

Since the stress developed in the external-most layer is independent of diffusivity and time, the initial crack, entering at right angles to the face, ought to form instantaneously if it is going to form at all. But it is otherwise as regards the extension of this crack to form a spall.

Griffith's[2] criterion for the ability of a crack to extend is this: that the strain energy released by the extension of the crack must be equal to, or greater than, the surface energy potentialized in the new surfaces produced. If an area of $2A$ sq. cms. of new surface is produced and the surface tension of brick is T, then the surface energy potentialized is $2AT$. This quantity is sensibly independent of the thickness of the spall, since the surface of separation is assumed to lie parallel to the face,[3] and the energy potentialized is much the same whether the spall is .001 or .1 inch thick.

But the strain energy set free is *not* independent of the thickness, but directly proportional thereto. At first the stress diagram is like ABC; after the lapse of a little time it is like ADC. The strain energy in unit volume is $\propto f^2/E$ and the volume containing this amount of energy is proportional to PD or PB. Hence the strain energy grows continually (in an infinitely thick slab) as the temperature gradient "soaks in." On splitting occurring through D, practically the whole of the strain energy is released. The initial crack after entering normally from the surface will therefore bend round parallel with the face and split through D, when D has soaked down far enough for the released strain energy to exceed the surface-energy required.

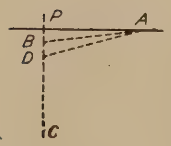

Fig. 5.

The depths at which the spall occurs would then depend on the surface-tension of brick and on the elastic modulus, but not on the diffusivity. On the other hand the time elapsing between quenching and spalling is a function of the diffusivity, since the rate of descent of D into the brick is given by $PD \propto \sqrt{kt}$ where k is diffusivity; or the critical time is proportional to $1/k$.

Standard Plate Glass Co.
Butler, Pa.

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[1] *Loc. cit.*, p. 38.

[2] A. A. Griffiths, *Phil. Trans., A.*, **221**, 163–98 (1920).

[3] Following Mr. Norton, we are considering an infinite slab.

A STUDY OF THE SHRINKAGE OF DIASPOR CLAYS.—PART I[1]

By S. M. Phelps[2]

ABSTRACT

Diaspor refractories often possess the undesirable characteristic of continual shrinkage in service, and since it is not practical to alter such properties in the present manufacturing processes, the object of this study was to devise, if possible, a manufacturing process to overcome this shortcoming. This part of the paper reveals the mechanism of the firing shrinkage and describes the effect of particle size, time and temperature upon the shrinkage of diaspor clays of various compositions. The properties of the two major constituents of a typical sample are given, as well as photomicrographs of interesting samples. Part II will describe experimental work conducted to devise shrinkage processes and the properties of products so made.

Introduction

Pure diaspor, being hydrous aluminum oxide, is only of mineralogical interest since no deposits of this material of any consequence exist in this country. However, in recent years diaspor-bearing clays[3] have been utilized in the manufacture of refractory products by reason of their many valuable inherent properties. In the Missouri clay districts it is commonplace to find pockets of refractory clay containing cores, which consist of clay high in diaspor.[4] This core of highly aluminous material is often of a sandy, burley nature and for many years was regarded as worthless or detrimental for use as a refractory material. Today such deposits are carefully worked and in many instances only the clays richest in diaspor are taken from the pits, since these pits occur scattered over a large area, and as they are comparatively small in tonnage, it is seldom economical to install mining machinery or a means of transportation to the railway. The materials mined are usually hand sorted to insure the securing of a highly aluminous raw material, which is calcined in many instances to facilitate a second and more careful separation.

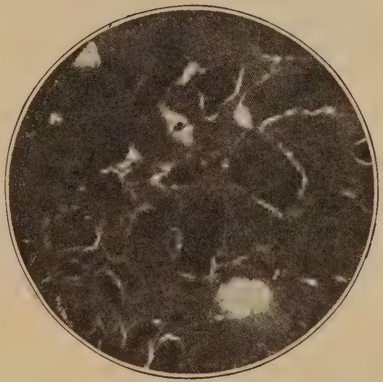

Fig. 1.—Photomicrograph of A diaspore after 1 reheat, showing grains of high alumina material.

The diaspor clays used commercially vary in alumina content from 50 to 80%, and in texture from a fine-grained, plastic clay-like nature to a coarse, gritty, short material. The diaspor is present in these materials principally as "oolites" of varying size and number, as is shown in Fig. 1. These particles of hydrous alumina are imbedded in a matrix of refractory clay material, the amount and nature of which govern to a large extent the characteristic of the mass, since it is virtually the bond of the aggregate.

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[1] Presented at the Annual Meeting of the American Ceramic Society, in Atlanta, Georgia, Feb., 1926. (Refractories Division.)

[2] Industrial Fellow, Refractories Fellowship, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

[3] The term "diaspor clay" will be used when describing this material, as suggested in the Missouri Bureau of Geology and Mines Biennial Report, pp. 17–20, State Geologist, Fiftieth General Assembly, 1919.

[4] Clays containing diaspor are found in other sections, notably Pennsylvania.

The reduction to a constant volume of aluminum hydrates has been the chief handicap in the utilization of these materials in refractory products. Howe and Ferguson[1] have shown the properties of diaspor, bauxite, and gibbsite, and point out the difficulty experienced in bringing about the maximum shrinkage.

Constancy of volume in service is one of the many requisites of refractory materials, and such a property is most difficult to secure in diaspor refractories, as the complete shrinkage of these clays by heat treatment alone would prove too costly for such a product. It is customary to manufacture this refractory by calcining to a high temperature a large portion of the diaspor used in the mix and bonding this with a suitable high alumina clay, and subsequently firing to a high temperature. Such brick show a constant volume in many high temperature uses, notably the hot zone of cement kilns; but when subjected to such extreme temperatures and especially after long periods of time, characteristic shrinkage cracks occur as shown in Fig. 2.

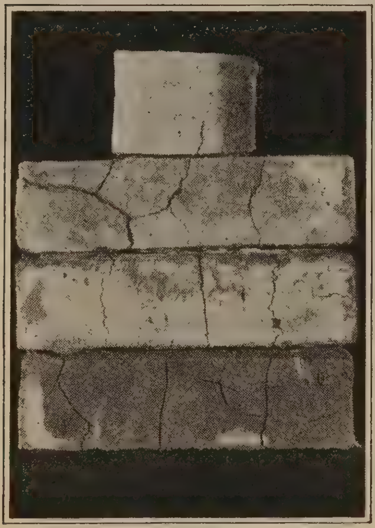

Fig. 2.—Showing shrinkage cracks as occurring in diaspor brick after long use.

Experimental

This study was principally to determine the cause and nature of this pronounced shrinkage, and, if feasible, to devise a procedure which would enable the producer to accomplish this result in the manufacturing process. For this study, large samples of typical diaspor clays were secured, which had the following physical and chemical properties:

Table I

Test	A	B	C
Fusion point	Above cone 36	Above cone 36	Above cone 36
Water of plasticity	27.6%	23.6%	14.50%
Drying shrinkage	9.20	11.60	3.90

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[1] *Jour. Amer. Ceram. Soc.*, **6**, 496–500 (1923).

TABLE I (*Concluded*)

Test	A	B	C
Volume shrinkage after 5 hours at 1400°C	24.3	24.4	15.20
Porosity after 5 hours at 1400°C	27.70	28.00	45.20
Soluble salts	.04	.03	.03
Chemical analysis—			
Ignition loss	13.46	14.32	14.20
Silica	28.36	9.40	2.56
Alumina	53.64	72.23	78.71
Iron oxide	0.56	0.59	1.58
Titania	2.80	2.92	2.75
Lime	0.12	0.31	0.28
Magnesia	0.26	0.23	0.34
Alkalis	0.97	0.93	0.29

To eliminate the grind factor in subsequent comparisons, these raw materials were ground to as nearly identical particle size as it is practicable to do with materials of this nature. The screen analyses of these samples were as follows:

TABLE II

	A	B	C		A	B	C
On 30-mesh	17.5	21.5	11.1	On 80-mesh	3.20	3.25	5.1
" 40- "	9.5	8.55	8.7	" 100- "	4.05	4.05	4.9
" 60- "	10.4	8.55	11.9	Through 100-mesh	55.35	54.10	58.30

Sample "A" was quite plastic, "B" less plastic and somewhat "mealy," and "C" was short and "mealy."

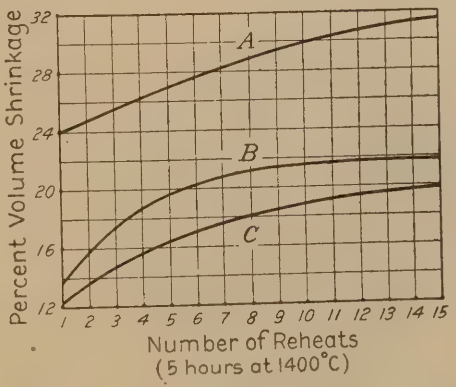

FIG. 3.—Showing effect of time at a given temperature upon shrinkage of various samples.

These clays were hand-molded into 2-inch cubes and the dry volume of these was determined by the use of the saturated and suspended weights in kerosene. After distilling off the oil by careful heating, they were fired and the resulting volume change calculated from the data obtained upon weighing them saturated and suspended in water.

The function of time in ceramic reactions is of great importance and this factor was studied in this work by repeated heatings at a given temperature. Each heating consisted of a standard reheat of 1400°C which is held for 5 hours. This temperature is reached in 4 hours and cone 15 to 16 is brought down in the test.

The data obtained after subsequent heatings of these diaspors are shown graphically in Fig. 3. It is evident from these curves that the duration of heating at a given temperature is of great importance in producing shrinkage and that the volume change is inversely in the order of the alumina present in these samples. These properties may be explained by the nature and quantity of the bonding portion and the particle size of the grains of the various materials.

An interesting experiment was conducted to study the difference in composition and firing properties of the bonding portion and grains of a sample of diaspor clay. The finely divided plastic constituents of the 20-mesh sample were separated by the aid of deflocculation, giving an arbitrary division. The portion containing the grains was very short and mealy and the fine material, which amounted to 16% of the total, was exceedingly plastic.

Cubes were molded of these constituents and given a reheating test with the following results:

	Porosity after reheating	Volume shrinkage
Fine material	18.4%	37.0%
Coarse "	52.5	10.8

These data are of value in explaining the behavior of such aggregates in heat treatment, especially the shrinkage relation to the alumina content.

Considerable difference in chemical composition exists in these components, as is evident from the following analyses:

	Grains	Bond	Original
Ignition loss	14.44	13.26	14.46
Silica	5.88	16.16	7.60
Alumina	77.06	62.13	73.70
Iron oxide	0.64	1.37	0.73
Titania	2.60	6.00	2.95
Lime	0.13	0.36	0.24
Magnesia	0.26	0.43	0.23
Alkalis	0.76	1.98	1.03
	101.77	101.69	100.94

The titania content of the bond sample is interesting since the alumina to titania ratio is about 10 to 1, which is nearly three times the amount that would be expected in a sample of this type.

The examination of thin sections prepared from samples of each diaspor after various periods of heating reveals many points of interest. Figures 1 and 4 show how the bond shrinks away from the grains as a result of one heating, whereas 15 reheats produce a sponge-like structure, as is shown in Fig. 5. Such a structure is produced by incipient fusion of the mass, thereby decreasing the viscosity of the glass formed, which in turn allows this liquid phase to draw the grains closer together by surface tension. This process would continue to a maximum density by prolonged heating, provided the viscosity of the glass is not increased. This probably takes place, however, by solution of the alumina in the glass until equilibrium is established, thus retarding the shrinkage.

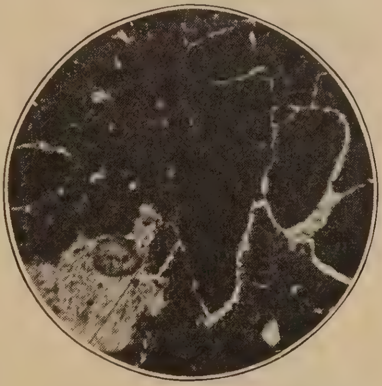

FIG. 4.—Photomicrograph of B diaspor after 1 reheat, showing grain of high alumina material.

Figures 6, 7, and 8 were taken with crossed nicols and show the relative amounts of crystalline material formed as a function of time at 1400 °C. Figure 6 shows "A" diaspor after 11 reheats and indicates in particular the large grain of diaspor which has started to crystallize, and progresses from the surface toward the center. Tridymite inversions in silica brick occur in this same interesting manner. This is shown again in Fig. 7, which also indicates the relative proportion of crystalline material developed after 1 and 11 reheats of "B" diaspor. It will be noted that the large grains of diaspor have not started to develop crystals after one heating, while these particles, after continued heating, are nearly all crystalline. This is likewise shown in "C" diaspor, Fig. 8, in which crystallization has progressed considerably as a result of continual heating. In this sample, the average grain size is much smaller than in "A" or "B."

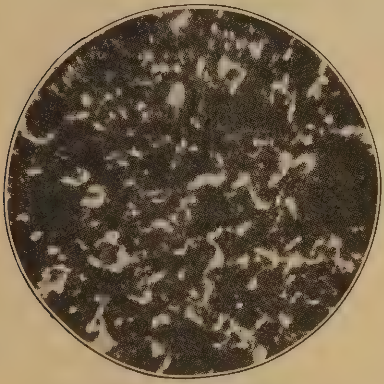

FIG. 5.—Photomicrograph of diaspor B after 15 reheatings.

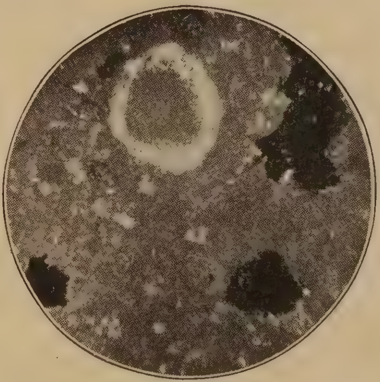

FIG. 6.—Photomicrograph taken between crossed nicols, showing crystallization of grains in B diaspor after 11 reheats. Note especially the large grain which shows progressive crystallization.

It was thought that the true specific gravity might be an index to the firing shrinkage, but after many careful determinations no significant relation between these properties could be formed, although an increase in specific gravity accompanies volume shrinkage. Table III presents these determinations, which were made upon 10-gram samples in Hogarth flasks.

TABLE III

	A		B		C	
	Volume shrinkage	True specific gravity	Volume shrinkage	True specific gravity	Volume shrinkage	True specific gravity
Green sample		2.91		2.97		3.17
After 1 reheat to 1400°C for 5 hrs.	24.3	2.97	24.4	2.99	15.20	
After 11 reheats to 1400°C for 5 hrs.	31.6	3.01	33.3	2.98	26.2	3.84
Ball mill sample 1 reheat					36.00	3.88

Average of 2 or more determinations

Diaspore, $Al_2O_3\,H_2O$	True specific gravity—3.3 to 3.5
Corundum	" " " —3.9 to 4.10

Upon increasing the temperature of firing, marked changes take place in structure as a result of the quantity of glass formed and the decreased viscosity of it. This is concluded from the data obtained upon heating samples "A" and "C" to 1500°C for 3 hours, in which treatment cone 26 was brought down. Even for short periods of time pronounced shrinkage occurs, provided the temperature is sufficiently high, as is shown as follows:

	A	C
Volume shrinkage—5 hrs, 1400°C cone 15–16	23.7%	12.1%
11 reheats, 1400°C 5 hrs.	31.6	26.2
3 hrs., 1500°C cone 26	30.0	21.0

To continue the study on the effect of temperature, arrangements were made through the courtesy of several concerns to have these diaspors fired to various temperatures under practical conditions. The data obtained from these tests are shown in Table IV and Fig. 9, and indicate again the importance of high temperatures in producing constant volume.

TABLE IV

	A		B		C	
Cone obtained in commercial firing	Per cent volume shrinkage	Per cent porosity	Per cent volume shrinkage	Per cent porosity	Per cent volume shrinkage	Per cent porosity
Cone 11	19	29.	7	43.0	3	48.3
12	21	28.5	11	43.2	6	49.1
16	22	26.5	13	41.2	10	48.2
17	23	26.7	15	40.1	12	47.3
20	24	27.0	25	37.6	16	42.7

It will be noted that "A," which has the greatest shrinkage and lowest alumina content, is brought to a maximum shrinkage at a lower firing temperature than either of the other samples. Diaspor "B," which is next in order in these characteristics, requires the next hardest firing, and "C," being highest in alumina, is the most difficult of all in which to affect constant volume.

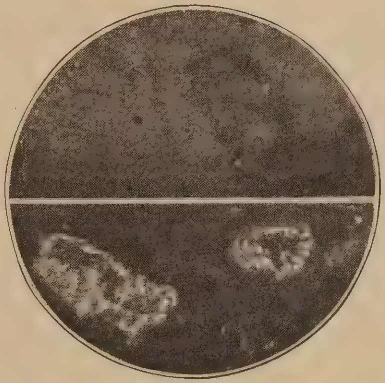

FIG. 7.—Photomicrograph of sample B taken between crossed nicols. Upper half after 1 reheat, lower half after 11 reheats, which shows the development of crystallized material after prolonged heating.

Since the shrinkage is affected by the nature and quantity of the glass in the mass during heating, any expedient which will alter these variables should effect its firing properties. Diaspor clay is a composite, composed of constituents possessing different chemical properties; and if these ingredients are ground to a fine state of division, reactions at elevated temperatures would be hastened. To study such a condition, samples of "C" diaspor were prepared with varying grinds of 20-mesh, 60-mesh and a ball-mill sample of exceedingly fine grind. Cubes of these materials were heated for 5 hours at 1400°C, producing the following volume changes:

20-mesh	9.18%	volume shrinkage
60-mesh	16.60	" "
Ball mill	36.00	" "

From these data it is evident that the degree of subdivision of such an aggregate in facilitating the reactions incident to shrinkage is of great importance.

The data derived from this phase of the study revealed information of a fundamental nature which proved to be of great help in the subsequent experiments, which were conducted to produce a permanent volume in aluminous refractories in the manufacturing process. The second part of this study will describe such experimental work and the properties of diaspor brick when made in accordance with the findings.

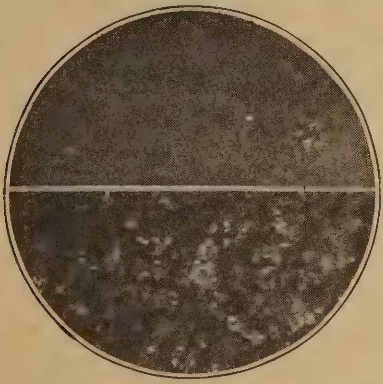

FIG. 8.—Photomicrograph of sample C taken between crossed nicols. Upper half after 1 reheat, lower half after 11 reheats, which shows the development of crystallized material after prolonged heating.

Conclusions

The shrinkage of the various types of diaspor clays under given conditions of time and temperature is inversely in the order of alumina content.

The duration of the firing period is of great importance in causing maximum shrinkage to take place.

The state of division is of importance in effecting shrinkage.

Great difference exists between the firing properties of the bond or plastic portion and the grains of diaspor.

Diaspor refractories should receive sufficient heat treatment during the manufacturing process to approximate a permanent volume or shrinkage will occur in service by the function of time or temperature.

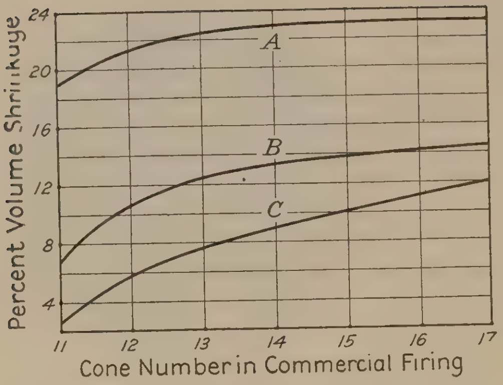

Fig. 9.—Showing effect of increased temperature upon the shrinkage of the various samples.

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Pittsburgh, Pa.

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SPECIFICATIONS FOR LINING AND CHECKER BRICK FOR WATER-GAS MANUFACTURE[1]

By E. J. Brady[2]

ABSTRACT

Specifications are given for all refractories used in water-gas manufacture based on U.G.I. experience. Description of equipment, operation, and conditions are given.

Since consumption of refractory products by the manufactured gas industries is approximately 5% of the total produced we especially thank your Program Committee for this opportunity to describe the needs of our industry, and to present for your consideration some tentative specifications for the purchase of refractory materials.

Although our quantity demands are small, our demands in regard to the character and quality of the refractories required equal, if they do not surpass, the demands of many of the larger consumers.

From the standpoint of the gas manufacturer, however, the problem of his refractories is one of major importance. The first cost is appreciable, but to this should be added the additional labor involved in removing the old and replacing the new, the wear and tear on the apparatus, the time lost during repairs, the reduction in output and the increase of unit costs.

The problem of increasing the life of gas works refractories lies no doubt with the ceramic engineers. The first step towards its solution is to explain in some detail the conditions which obtain in a carbureted water-gas set during the process of making gas. As a preface to the proposed specifications, we give a series of drawings showing how the refractory material is disposed in a water-gas set, the temperatures to which the different parts of the apparatus are subjected, and the character of the gases, with their velocities, qualities, and content of abrasive material.

The Water-Gas Set and Operation

The water-gas process is essentially cyclical. A fuel bed is blasted with air until the most intense combustion possible is attained. This is quickly changed to a condition in which comparatively cold steam, sometimes not superheated, passes over the same surface, with its great capacity for carrying away heat. This cycle is repeated every 4 or 5 minutes.

During this blasting period, the producer gas at 1200 to 1300°F passes into the carbureter, and on the way "secondary air" is added for combustion in the checker work, where a temperature of 1600 or

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division.)

[2] The Physical Laboratory of the U. G. I. Contracting Co.

1700°F may be obtained. Immediately afterwards a comparatively cold carbureting oil is sprayed over and among the same checkers.

The large masses of clinker adhering to the lining of the generator are removed with a long heavy bar, and this may or may not break off portions of the brick. Operators have been known to flood the bottom part of the generator with water to expedite the removal of the clinker. In the connections between the various vessels of the set, brick, if at all underfired, have been known to wear away in a few days' operation, due to the abrasive action of high velocity gases at high temperatures carrying particles of ash and carbon.

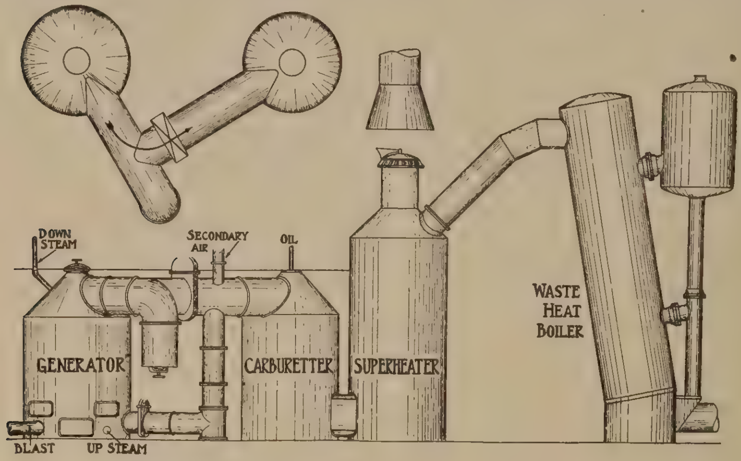

Fig. 1.—General view of a U. G. I. carbureted water-gas set. (Diagrammatic).

A recent marked improvement in the production of water gas using bituminous coal as fuel calls for a pier or column of refractory material in the center of the generator. This pier is surrounded on all sides by the incandescent fuel during blasting, and the temperature gradient, if any, in the material of the pier is probably small. This may ultimately prove to be a severe service for refractory material.

During the blasting period, air is blown into the bottom of the generator at a rate of 13,000 cubic feet per minute. The producer gas thus formed passes from the generator to the carbureter with a velocity of 10,500 feet per minute. This gas is composed of 12% CO_2, 11% CO, and 77% N_2. It has a temperature of 1200°F, and carries approximately two pounds of ash and coke breeze per minute. The erosion caused is sometimes severe, especially at the bends in the connection. (See Fig. 2).

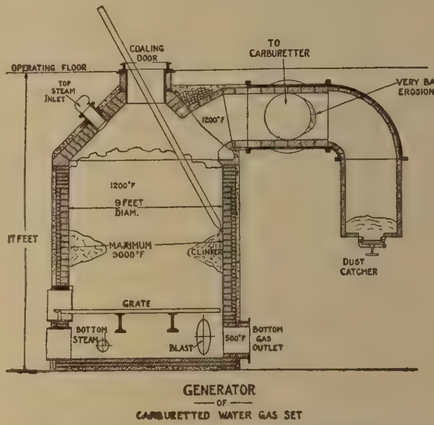

Fig. 2.—Cross-section through the generator.

Secondary air is added at this point, and combustion takes place in the checker work of the carbureter. The temperatures there may be 1450 to 1700°F, and the downward velocities of the gases are approximately 2900 feet per minute.

The resulting products pass through the lower connection to the bottom of the superheater with a velocity of 6600 feet per minute, and a temperature of 1450°F. The composition of these products is N_2 80.64, CO 0.15, CO_2 18.57 and O_2 .64. They then pass upwards through the checker brick of the superheater with a velocity of 2500 feet per minute, and with a temperature at the bottom of 1450°F, and at the top of 1400°F, thence to the waste heat boiler, which is lined with refractory material at the top only. The refractory lining is subjected to severe corrosion at all of these connections.

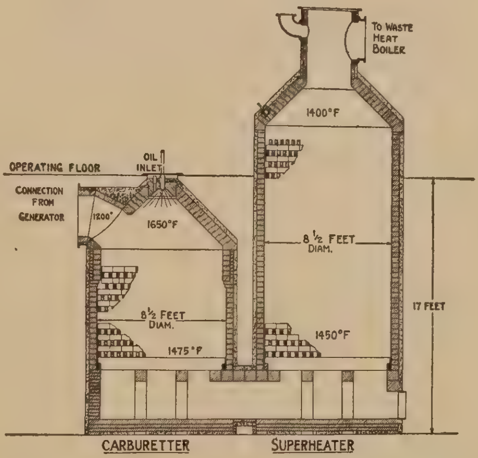

FIG. 3.—Cross-section through the carbureter and superheater.

During the "run," the part of the cycle during which steam is decomposed by the fuel bed previously heated by the blast, steam is admitted to the bottom of the generator at the rate of 225 pounds per minute. This passes up through the fire, and the resulting gas is composed approximately of 43.5% CO, 47.3 H_2, 0.7 CH_4, 3.5 CO_2, .6 O_2 and 4.4 N_2. This passes through the same connection to the carbureter with a velocity of 3000 feet per minute, and a temperature of 1200°F.

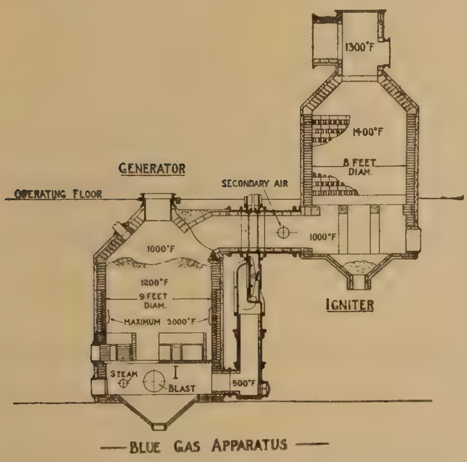

FIG. 4.—Cross-section through a blue gas generator with igniter. (Diagrammatic).

At the beginning of the "run" oil is sprayed into the top of the carbureter at the rate of 50 gallons per minute. (See Fig. 3). This trickles down through the checker work and is vaporized and there it is decomposed by the high temperature. This chills off the checker work very rapidly, sometimes producing excessive spalling, especially after the checker brick become impregnated with carbon. Gases seem to penetrate these bricks, and they are decomposed in the interstices, leaving the carbon behind. When thus impregnated with carbon the bricks spall very badly.

Steam is sometimes admitted at the top of the generator, passing down through the fuel, and thence through the carbureter and superheater, as above described. Various modifications of the operation of the set are used, but this description is sufficient to give a general idea of the conditions obtaining in the average water-gas set.

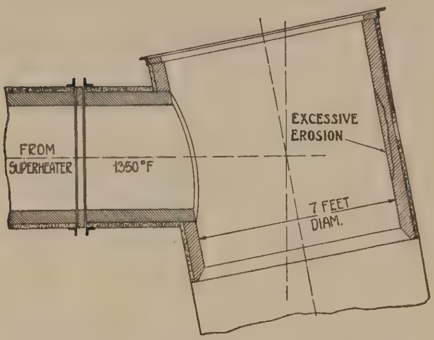

FIG. 5.—Cross-section through the top of a waste heat boiler.

Blue Gas Where "blue gas" or uncarbureted water gas is made, the operation is as described, but instead of a carbureter, the blast passes through an ignitor, (see Fig. 4), a large refractory-lined chamber similar to the carbureter, and containing checker work. From there it passes to the waste heat boiler. (See Fig. 5).

Analysis of Coke Ash and Clinker A representative analysis of the ash of coke is as follows:

	Per cent		Per cent
Silica	55.1	Magnesia	1.2
Iron and alumina oxide	39.4	Sulphuric acid	0.41
Lime	3.4	Undetermined	0.49

A typical clinker, which adheres to the lower part of the generator lining, has approximately the following composition:

	Per cent		Per cent
Iron silicate	22.18		
(Iron oxide 5.88%		Metallic iron	0.71
Silica 16.3%)		Ferrous oxide	1.6
Silica	33.15	Ferric oxide	16.82
Titanic acid	1.22	Calcium oxide	1.75
Alumina	22.2	Traces of magnesium	

It will be seen from the foregoing that in the manufactured gas industry the ceramic engineer has a field of endeavor worthy of his very best effort, and I am sure that once the problem is understood he will draw upon his experience along similar lines, and valuable suggestions will be forthcoming.

The following specifications have been prepared by a committee of engineers of the U. G. I. Contracting Company. Their object is to bring about a more systematic method of selecting and purchasing refractories, and principally to enable the Company ultimately to select the very best refractory for the service intended.

Specifications for Refractories

Explanation of the Specifications In order to let the vendors of the various refractory products know the requirements of the U. G. I. Contracting Company in regard to the refractory products used in the manufacture of gas, and to provide standard methods of selecting and testing refractory products submitted to the U. G. I. Contracting Company by the manufacturers of such products, the following general specifications have been prepared.

They apply only to fireclay products, used in apparatus for the manufacture of gas, such as generators, carbureters, superheaters, waste heat boilers, and ignition chambers, but not to steam boiler practice.

They apply to the selection and testing of the finished product only, and not to the quality of the material entering into the product, nor to the methods used in the manufacture thereof.

Refractory material may differ in the following respects:

Appearance,	determined by observation
Size and shape,	determined by measurement
Composition,	determined by chemical analysis
Behavior under test,	determined by physical test

The different duties for clay and siliceous clay refractory products purchased by the U. G. I. Contracting Company for water-gas sets are as follows:

Duty	Tests Which May Be Applied
Generator lining fire zone	Load, porosity, slagging, and softening point
Generator lining upper zone Also: carbureter lining, and blue gas igniter	Load, porosity, slagging, and softening point
Tees and connections Also: waste heat boiler	Spalling and abrasion
Checker brick for carbureter and superheater.	Spalling and porosity
Special cements for clay products	Softening point, abrasion, joint and patch
Cement for clay products low temperature non-abrasive	Softening point, abrasion, joint and patch

In the following there will be found an individual specification for each of the services or duties. Each specification is divided into four parts, the parts covering the four ways in which the product can differ, as mentioned above. Under each heading the permissible limitations are stated, and where the method of determining these limitations require explanation, such as "composition" and "behavior under test," parenthetic reference will be made to one of a series of appendixes attached to the specifications. In these appendixes will be found a detailed description of the manner in which the "composition" or "behavior under test" shall be determined.

Fireclay Products for Generator Lining

Fire Zone.—(Class H 80 A. S. T. M. Service Classification.)

Appearance.—The material for the above service shall have a good and even texture reasonably free from flaws, such as cracks, voids or soft centers, and it shall be evenly fired throughout.

Size and Shape.—The standard shape bricks shall have their corners of the proper angular dimensions, be free from warps, with full edges and corners.

The thickness of any single brick shall not differ from $\frac{1}{10}$ of the height of 10 bricks laid one on top of the other by more than 3% ±.

The length of any single brick shall not differ from $\frac{1}{10}$ of the length of 10 bricks laid end to end by more than 1% ±.

The width of any single brick shall not differ from $\frac{1}{10}$ of the width of 10 bricks laid side by side by more than 2% ±.

The 10 bricks for the above measurements shall be picked at random from the pile, and the measurement may be repeated at the discretion of the inspector to ascertain the average.

Special shapes, for the above service, must conform to the drawings furnished by the U. G. I. Contracting Company, and unless special limits of tolerence are shown in the drawings no dimension shall vary more than $\frac{1}{8}$ inch ± that shown, excepting that shapes having a dimension exceeding 6 inches may have a variation in proportion to $\frac{1}{4}$ inch per foot. Pieces not complying with the above shall be rejected.

Composition.—The material shall contain not less than 37% alumina, (Al_2O_3).

Behavior under Test.—Load Test (See Appendix A).—The expansion during (*a*) shall not be greater than 2%, approximately $\frac{3}{16}$ inch on a 9-inch brick.

The temperature during (*b*) shall not be less than 2550°F.

The contraction during (*b*) shall not be greater than 10%, approximately $\frac{7}{8}$ inch on a 9-inch brick.

Softening Point and Slagging Test (See Appendix B).—The temperature at which the pure brick cone begins to turn will be called the softening point. This temperature shall not be less than 3000°F.

The temperature at which the ash-brick cone begins to turn shall not be less than 2900°F.

Porosity Test (See Appendix E).—The porosity of this material shall be not less than 15%, nor more than 22% for standard bricks, and not more than 28% for the large shapes.

Fireclay Products for Generator Lining

Upper Zone.—(Class M 17 A. S. T. M. Service Classification.)

Appearance.—The material for the above service shall have a good and even texture reasonably free from flaws, such as cracks, voids or soft centers, and it shall be evenly fired throughout.

Size and Shape.—The standard-shape bricks shall have their corners of the proper angular dimensions with full edges and corners.

The thickness of any single brick shall not differ from $\frac{1}{10}$ of the height of 10 bricks laid one on top of the other by more than 3% ±.

The length of any single brick shall not differ from $\frac{1}{10}$ of the length of 10 bricks laid end to end by more than 1% ±.

The width of any single brick shall not differ from $\frac{1}{10}$ of the width of 10 bricks laid side by side by more than 2% ±.

The 10 bricks for the above measurements shall be picked at random from the pile, and the measurement may be repeated at the discretion of the inspector to ascertain the average.

Special shapes, for the above service, must conform to the drawings furnished by the U. G. I. Contracting Company, and unless special limits of tolerance are shown in the drawings no dimension shall vary more than $\frac{1}{8}$ inch ± that shown, excepting that shape having a dimension exceeding 6 inches may have a variation in proportion to $\frac{1}{4}$ inch per foot. Pieces not complying with the above shall be rejected.

Composition.—The material shall contain not less than 37% alumina, (Al_2O_3).

Load Test. (See Appendix A).—The expansion of a 9-inch standard brick during (*a*) shall not be greater than 2%, approximately $\frac{3}{16}$ inch.

The temperature during (*b*) shall not be less than 2400°F, (cone 13).

The contraction of a 9-inch standard brick during (*b*) shall not be greater than 10%, approximately $\frac{7}{8}$ inch on a 9-inch brick.

Softening Point and Slagging Test (See Appendix B).—The temperature at which the pure brick cone begins to turn will be called the softening point. This temperature shall not be less than 3000°F.

The temperature at which the ash-brick cone begins to turn shall not be less than 2750°F.

Porosity Test (See Appendix E).—The porosity of this material shall be not less than 15%, nor more than 35%. This applies to both standard brick and shapes.

Fireclay Products for Lining Tees and Connections

(Class M 51 A. S. T. M. Service Classification).

Appearance.—The material for the above service shall have a good and even texture reasonably free from flaws, such as cracks, voids, and soft centers, and it shall be evenly fired throughout.

Size and Shape.—The standard-shaped bricks shall have their corners of the proper angular dimensions with no warps, and with full edges and corners. The dimensions shall not vary from the standard values, or from the drawing furnished for these pieces by more than 2% ±.

Composition.—The material shall not contain more than 60% silica (SiO_2).

Spalling Test (See Appendix C).—The bricks for this service shall withstand six quenchings without failure.

Abrasion Test (See Appendix D).—The bricks for this service shall have an abrasion factor not greater than 100.

Fireclay Products Checker Work

(Class M 50 A. S. T. M. Service Classification).

Appearance.—No requirements.

Size and Shape.—The brick shall be rectangular in shape with full edges and corners. The width of any single brick shall not differ from $\frac{1}{10}$ the width of 10 bricks laid side by side by more than 2% ±.

Composition.—The brick for this service shall contain not more than 60% silica, (SiO_2).

Spalling Test (See Appendix C).—The material for this service shall withstand 10 quenchings without failure.

Porosity Test (See Appendix E).—The bricks for this service shall have a porosity not less than 20%, and not greater than 30%.

Special Cements for Fireclay Products

Appearance.—No requirements.

Size and Shape.—The material shall be such that, when it is prepared for use according to the vendor's instructions, it shall have the proper plasticity for good working with the trowel.

Composition.—No requirements.

Softening Point Test (See Appendix B).—The softening point of the material for this service shall not be less than 2700°F.

Abrasion Test (See Appendix D).—The material, after firing in the joint and patch test, shall have an abrasion factor of not more than 120.

Joint and Patch Test (See Appendix F).—The material shall be able to withstand a constant temperature in this test of not less than 2550°F and its cementing and patching qualities must be satisfactory.

Special Cements for Low Temperature Non-Abrasive Fireclay Products

Appearance.—No requirements.

Size and Shape.—The material shall be such that, when it is prepared for use according to the vendor's instructions, it shall have the proper plasticity for good working with the trowel.

Composition.—No requirements.

Softening Point Test (See Appendix B).—Softening point of the material for this service shall not be less than 2200°F.

Abrasion Test (See Appendix D).—The material should set at a temperature below 1300°F, and after firing at 1400°F, it should have an abrasion factor of not more than 140.

Joint and Patch Test (See Appendix F).—The material shall have a good air set, and adhere to the brick and it shall be able to withstand a constant temperature in the joint and patch test of not less than 2000°F and its cementing and patching qualities, after this test, must be satisfactory.

Appendix A
Load Test

This test is to be performed in a load test furnace constructed in accordance with the A.S.T.M. Specification (Serial C–16–20, see page 737—A.S.T.M. Standards 1924), and the test itself conducted in accordance with those specifications, except in the following respects.

For purposes of description the modified test may be divided into three periods.

(*a*) The temperature will be increased at a rate to correspond as nearly as practical with the temperatures given under the column headed "heavy duty" on page 738 of the above volume. This rate will be adhered to on all fireclay products.

(*b*) When the temperature will have reached a point where the expansion of the specimen ceases and contraction has definitely set in, further heating will be stopped, and the temperature attained will be held constant as nearly as feasible for 1½ hours.

(*c*) At the end of 1½ hours the heating method will be so adjusted that the temperature of the furnace will, as nearly as feasible, resume the rate of increase it had when the 1½ hour constant temperature period began, and the temperature of the furnace will be increased indefinitely until the specimen either collapses or shows a contraction of 3 inches, when the supply of heat will be cut off and the furnace allowed to cool.

Appendix B
Slagging and Softening Point Test

A portion of the brick will be ground, and all of it passing through a standard 60-mesh sieve saved.

A selected sample of the ash of the coal or coke to be used in the installation will be ground, and all of it passing through a standard 60-mesh sieve saved, or a standard ash for this purpose may be used in the judgment of the Company.

A mixture of 70% of the above brick material and 30% of the ash material (by weight) will be moistened with a 10% dextrine-water solution, and formed into cones, similar to the Orton cones, ¾ inch long.

Cones of the brick material alone will be similarly formed with some of the above solution.

One each of the above two kinds of cones will be stood side by side on a plaque, and allowed to dry for 24 hours. The whole will then be placed in a carbon tube electrical resistance furnace, (through which hydrogen is slowly passing) and heated gradually. During the critical period, the rate of increase will not be greater than 30°F per minute.

The temperature (by optical pyrometer) of the first turning of the ash-brick cone will be recorded, and later the first turning of the pure brick material cone, if this takes place below 3200°F. If the latter does not turn before 3200°F, the test will be discontinued at that temperature

The temperature at which the ash-brick cone begins to turn will be the primary factor. The difference of the two temperatures, *viz.:* the temperature of the first turning of the pure brick cone minus the temperature of the first turning of the ash-brick cone, will be a secondary factor.

Appendix C

Spalling Test

The specimen will be prepared for test by heating uniformly under no load at 2550°F for five hours, and allowing to cool slowly to room temperature.

The end of the brick will then be heated by placing the brick in the side of a suitable furnace, which is being held at a temperature of 2460°F.

The heated end of the brick will be kept flush with the inner wall of the furnace, and the outer end should be exposed to the free circulation of the air. The hot gases are to be prevented from issuing around the brick.

At hourly intervals the brick is to have its hot end immersed in running water for three minutes, and to a depth of four inches.

The brick will then be removed, allowed to steam in the air for five minutes, and returned to its opening in the wall of the furnace.

This cycle will be repeated until the specimen fails.

The brick will have failed in this test when the heated end is completely spalled away, or when the structure of the brick has become so weakened that it can be easily removed with the hand.

Not less than three specimens of any one brand to be operated upon, and the average numbers of immersions of all specimens operated upon will be taken and called "the number of immersions."

Appendix D

Abrasion Test

Four bricks will be laid on their sides in a horizontal position with a corner of each in close juxtaposition. They will lie with their upper surfaces 19 inches below a vertical sand blast nozzle $\frac{3}{8}$ inch in diameter. One of the four bricks used is to be a "comparison brick" of some well known brand.

Air of 30 pounds pressure per square inch will be supplied to the nozzle for three minutes, and during that time 10 pounds of a good clean building sand of 20-mesh will be fed into the issuing stream of air.

After the above treatment, the volume of the eroded depression at the corner of each of the four bricks will be measured.

The volume of the eroded depression in the "comparison brick" will be given an arbitrary value of 100, and the erosion of the other bricks will be expressed in terms of this, as follows:

Erosion factor = V_x/V_c 100, where V_c is the volume of the eroded depression in the "comparison brick" and V_x that of the brick under test.

The method of measuring the above volume consists in filling the depression flush with a fine grade of silica sand, and weighing this sand on a chemical balance.

Appendix E

Porosity Test

The porosity will be determined on a porosimeter similar to the "Washburn-Bunting" apparatus.[1]

The porosity of one or more representative samples of the brick will be measured and the average determination taken.

The volume of the brick will be determined from the average of a number of measurements made on the three dimensions.

Air will be used as the pore filling agent.

The vessel containing the brick is evacuated approximately to 20 mm. pressure of mercury, the pressure on this and on a smaller glass vessel of known volume is read, then a stop-cock communicating with the smaller vessel of known volume and pressure is opened. After the air has penetrated into the interstices of the brick, the common pressure on both vessels is read.

From the data so obtained the porosity of the brick will be calculated.

Appendix F

Joint and Patch Test

The cement will be mixed in accordance with the directions received from the vendor.

Five half bricks of good quality will be cemented together, one upon the other, making a column approximately 13 inches high. The upper joint will be made $\frac{1}{16}$ inch thick, the next joints below in order $\frac{1}{8}$, $\frac{3}{16}$ and $\frac{1}{4}$ inch thick.

The bats in this column will be so placed that the fractured end of each is on the same side of the column, thus providing a rough surface upon which a patch of the cement will be made.

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[1] *Jour. Amer. Ceram. Soc.*, **4,** 536 (1921).

This column, after being allowed to dry for two or three days, will be placed in the furnace under a load of ten pounds per square inch, and the temperature increased in accordance with a heavy duty curve of the A.S.T.M. Specification (Serial C–16–20, page 740, 1924 Standards) until the joint material begins to bulge out, but does not run down the side of the brick. The temperature of the furnace will then be held practically constant for one hour. The average temperature during this hour, the general appearance of the material after test, and the manner of bonding with the brick will determine its suitability for the service expected.

Conclusion

Many of the large brick manufacturers have excellently equipped laboratories for testing their products. Tests are being simplified and made less costly.

It is hoped that this practice will become more general, and that even the smaller companies will secure equipment necessary to perform some of the tests called for by various specifications. The intelligent use of such equipment by both the purchaser and the manufacturer, and a willingness to coöperate on the part of both is the only way in which we can obtain the ultimate object of all specifications and tests, *viz.:* greater efficiency.

1401 Arch St.
Philadelphia, Pa.

REDESIGNED DRIERS[1]

By Hobart M. Kraner and A. H. Fessler

ABSTRACT

Inefficient driers used for drying dry-press porcelain were converted into flexibly controlled, efficient driers with a minimum of expense. Changes in handling, ware routing, etc. were thus averted.

A need for more drier capacity in a dry-press porcelain plant forced consideration of redesigning. To add driers would entail crowding of space, rerouting of ware, extra handling, etc. Making the available driers more efficient seemed to be the logical move. Considering the types being used, this was an extremely simple problem. Inasmuch as this type of drier is so much used, the solution of the problem may be of general interest.

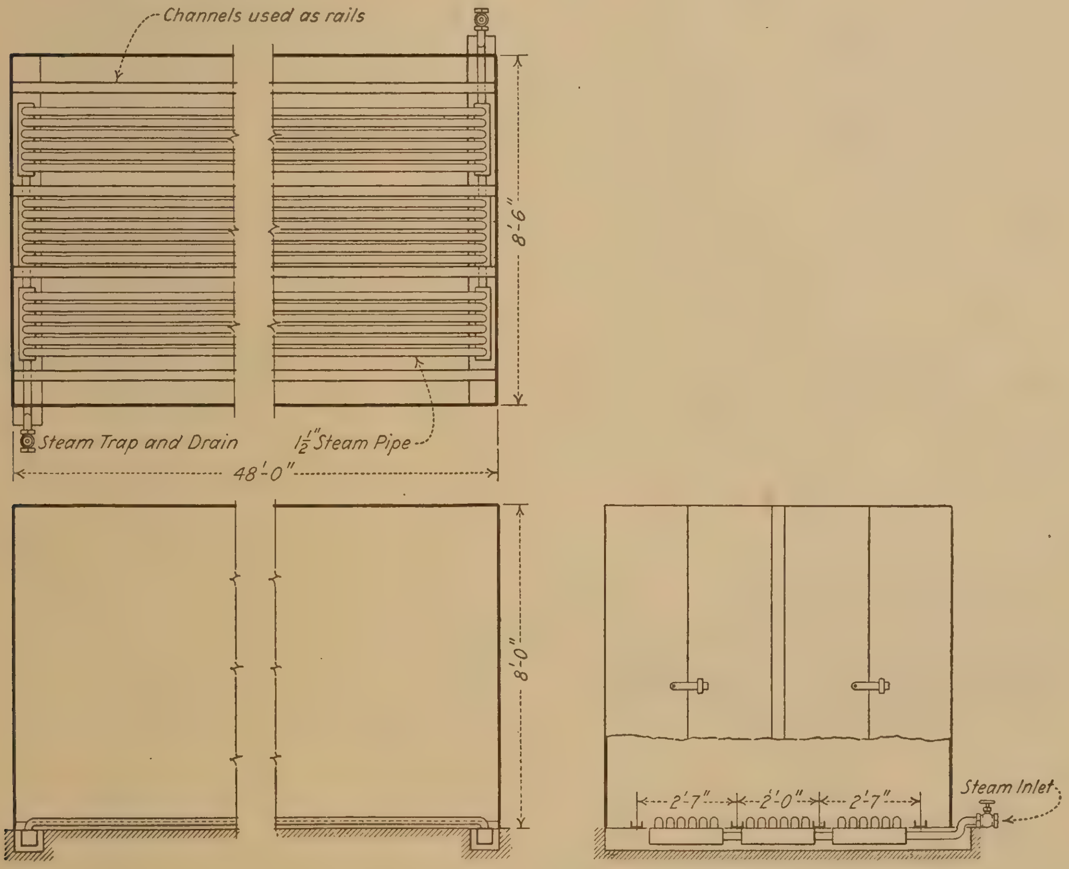

Fig. 1.—Original drier.

Figure 1 represents a drier which contained two steam coils of 828 feet of 1½-inch pipe using 120 lbs. per square inch steam pressure. These coils were laid directly on to the concrete floor. Very little heat was obtained by radiation as the lowest shelf of the cars was

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (White Wares Division). Received January 13, 1926.

14 inches above the pipes. Circulation also was poor with the result that 5 days was the usual drying period.

Figure 2 represents the same drier after remodeling. The height of the drier had been much greater than necessary and provided a large waste space over the cars of ware. By placing the old steam coils between a false ceiling and the original ceiling, this waste space was converted into a chamber through which air could be drawn for heating and blown through the ware. This circulation was done by means of a 36-inch propeller blade fan. Eight-pound exhaust steam was substituted for the 120-pound steam in the heating coils.

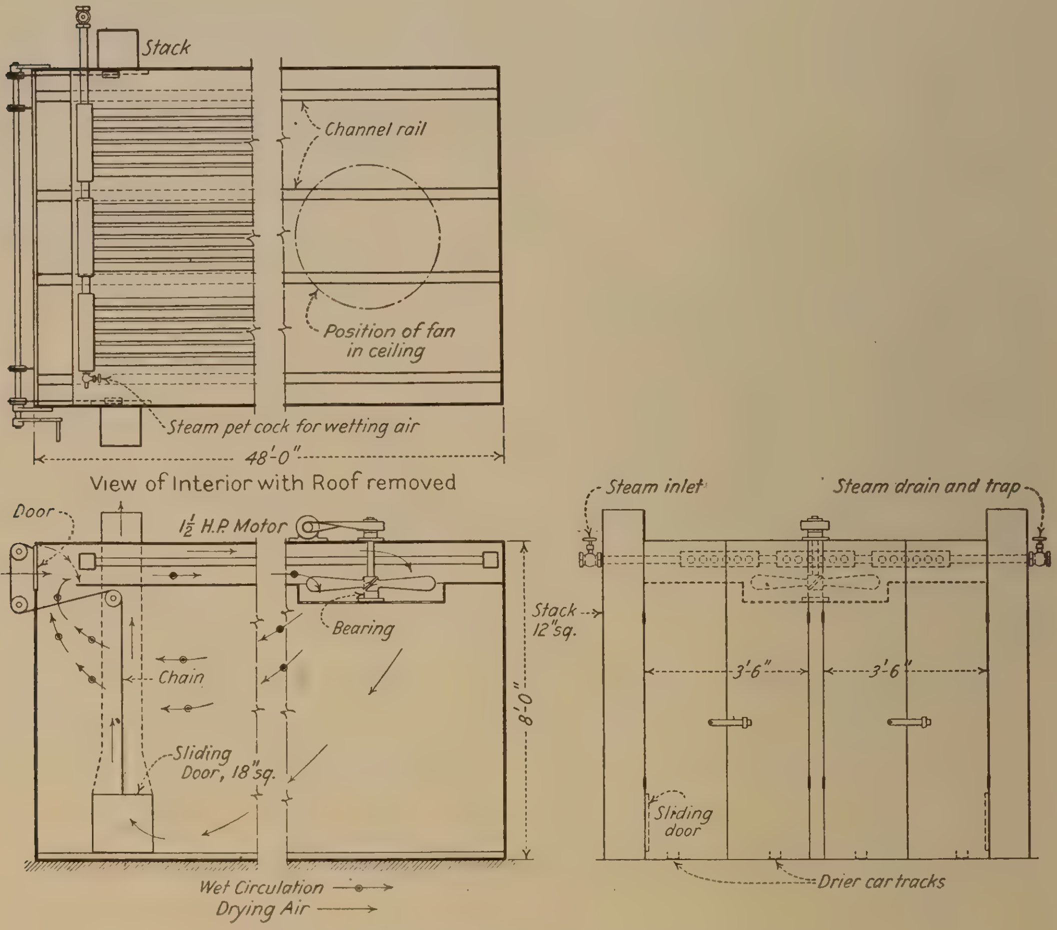

FIG. 2.—Remodeled drier, showing circulation.

The mechanism at the charging end was controlled by a single operation whereby recirculation with no intake or exhaust of air, intake and exhaust only, or any intermediate condition could be obtained to suit the conditions to be met from time to time or as determined to give satisfactory permanent drying schedules.

Safe drying was done in the remodeled drier with the drying time reduced to as little as 25% of the original time.

Figure 3 represents a ware drier in which high pressure steam pipes were placed beneath a slat floor. The ware boards were stacked one upon another on this floor. The circulation, if any, took place vertically between the stacks of ware and was therefore ineffective. Dust and broken ware which had fallen through onto the pipes often insulated them. Dry-pressed ware containing an average of only 14% water should dry safely in a much shorter period than was necessary in this type of drier, namely 5 days.

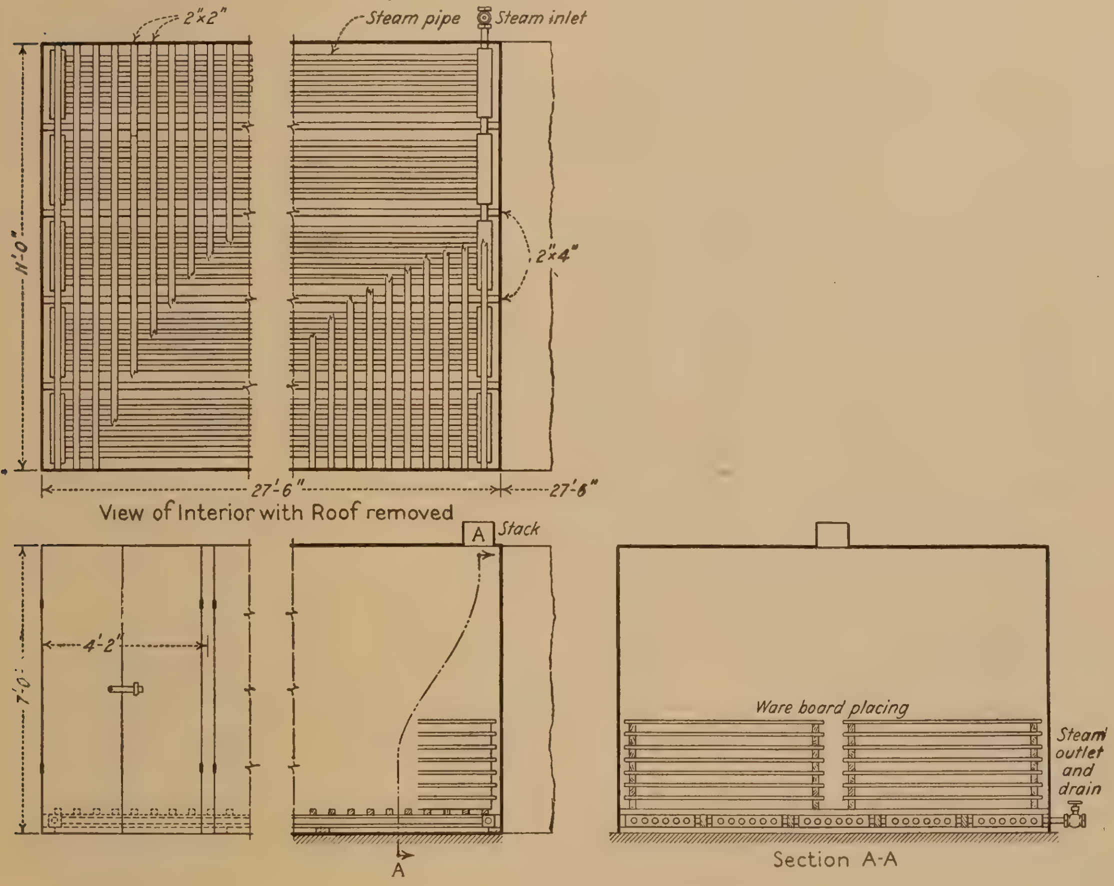

FIG. 3.—Original drier.

In Fig. 4 the same construction was used except that the floor and steam pipes were removed. Low pressure steam coils were placed in the end. A 30-inch propeller blade fan was used to produce circulation through the coils and ware. The blast of air driven horizontally effected drying more readily than the small amount of circulation obtained in the original drier. When driven horizontally through ware it could reach each board of ware. The outside wall, inside wall, and baffle contained openings at such positions as to permit control of conditions just as in Fig. 2. One operation changed the conditions from recirculation of moist air to that of circulating dry air through the ware and out of the drier, or any intermediate condition.

The removal of the slat floor made this drier adaptable to drier car use. Four and five days had been used in drying ware. The new schedule was two days. A slower schedule could be used where pieces were to be dried slowly. It was with this in mind that the flexibility sought through the recirculation of wet air and the provision for a simple way of reducing the humidity was considered.

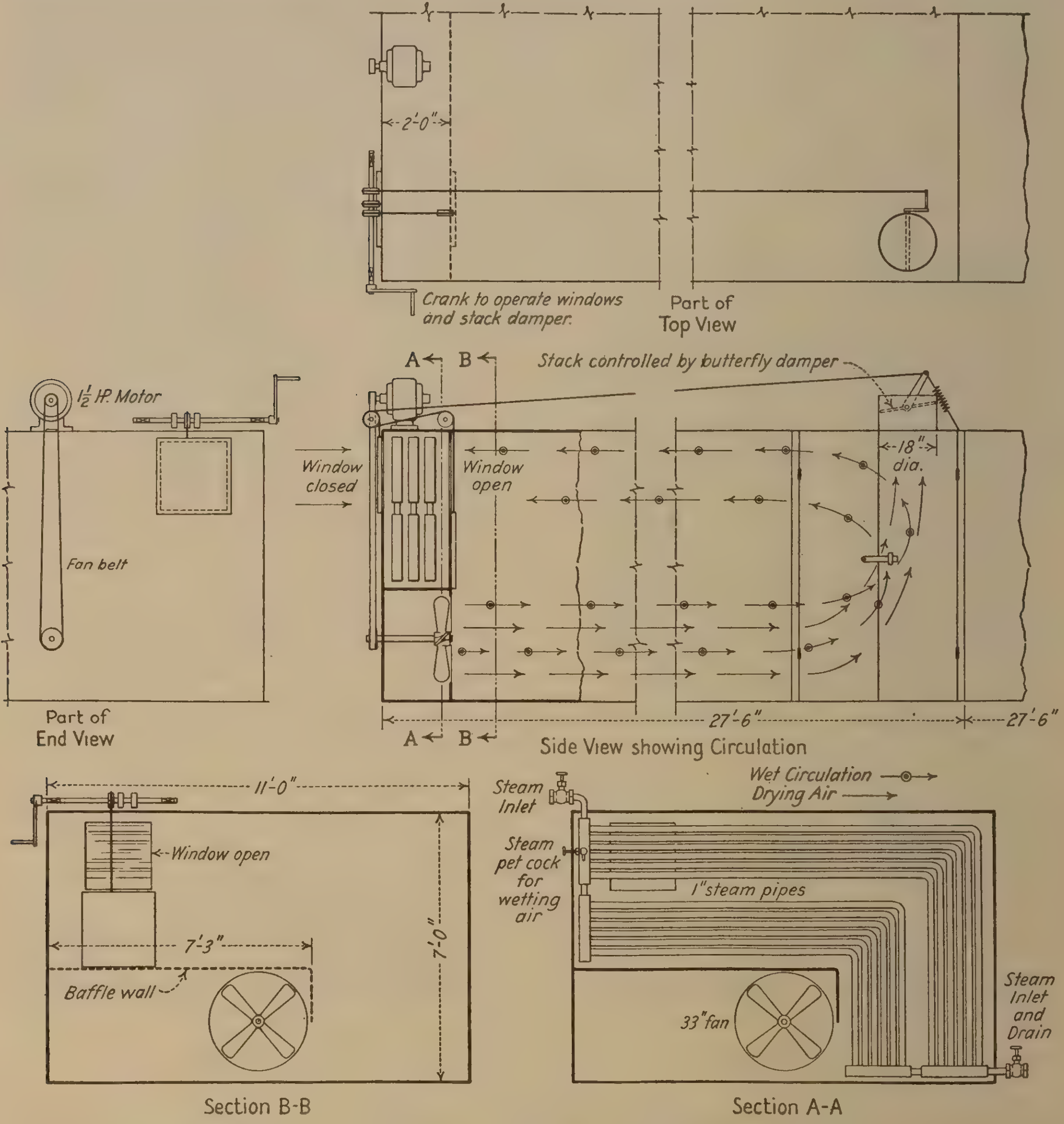

FIG. 4.—Remodeled drier.

Conclusions

1. Due to the fact that no data are available on the steam consumption of any of these driers and that assumptions used for cal-

culation would be full of error, the economy of operation cost of one over the other is in question. The remodelled types each use 1½-horse power motors running continuously. They, however, use low pressure exhaust steam which had not been previously utilized in this instance. This latter saving no doubt offsets the cost of motor operation.

2. It is believed that the faster drying schedule and the flexibility of drying control were obtained most easily and cheaply in the manner described.

3. The drying problem was solved effectively in this case.

Westinghouse Electric and Manufacturing Co.
East Pittsburgh, Pa.

A SUCCESSFUL APPLICATION OF POWDERED COAL AS A TUNNEL KILN FUEL FIRING HARD FIRED COMMON BRICK[1]

By Frank M. Hartford

ABSTRACT

The application of powdered coal by means of a non-circulating unit system to the successful firing of common brick in a continuous car tunnel kiln.[2]

Before getting into the main part of this subject it is desirable that the practical problem of tunnel kiln firing be discussed in relation only to the furnace section of the kiln. This preliminary discussion does not permit touching on the problems encountered in the water-smoking section, the preheating section or the cooling section of the kiln. It is sufficient in regard to these other sections of the kiln to say that the problems are being met and solved as rapidly as they arise. There are many problems but the success attained to date in the treatment of common brick, face brick, hollow tile, ladle brick, and fire brick bids well for their solution when encountered.

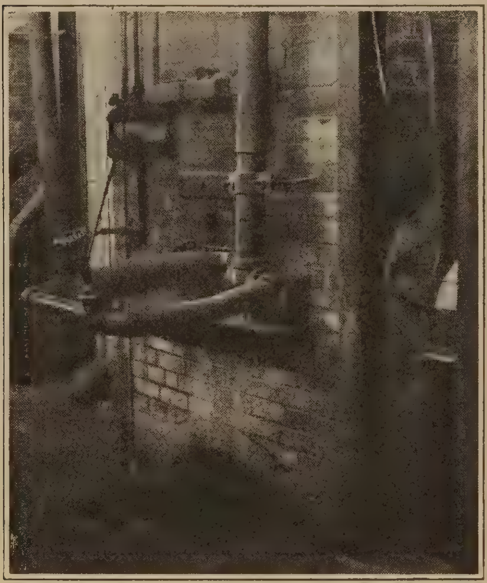

Fig. 1.—A close-up of furnace front which shows the burner arrangement in detail. The vertical pipe at the left is carrying the coal and air mixture from the proportioning fan to the burner. The vertical pipe in the center is carrying secondary burner air, which is introduced at the rear of the burner and mixes with the stream of coal and air coming from the proportioning fan. The entire mixture is then shot into the furnace.

To focus on the furnace section problem, the simplest form of a firing zone must be visualized as one in which the furnaces are disposed along the sides of the tunnel on $8\frac{1}{2}$- to 12-foot centers, and five, six, or seven furnaces on each side of the kiln, the position of the furnaces on one side being in staggered relation to those on the other side.

The problem is to get a large tonnage of ware through the furnace section and have the setting evenly fired from side to side and from top to bottom. The cross-section of the setting is only about $5\frac{1}{2}$ feet square, but 24 to 30 cars of ware every day must be passed through this furnace section which means from 100 to 125 tons of fired ware per 24 hours.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Heavy Clay Products Division.) Received Aug. 10, 1926.

[2] At this time of publication the kiln is producing 38 cars of ware per day. This is approximately 76,000 brick per 24 hours.

Heat alone can be secured from almost any fuel. No. 1 ware capacity depends on the ability to make proper use of this heat. Penetration into the heart of the setting must be positive with minimum danger of overfiring of the outside of the setting. The longer firing range clays present an easier problem than the short range clays in this respect but that which is good practice on the short range clays will result in greater tonnage on the longer range clays.

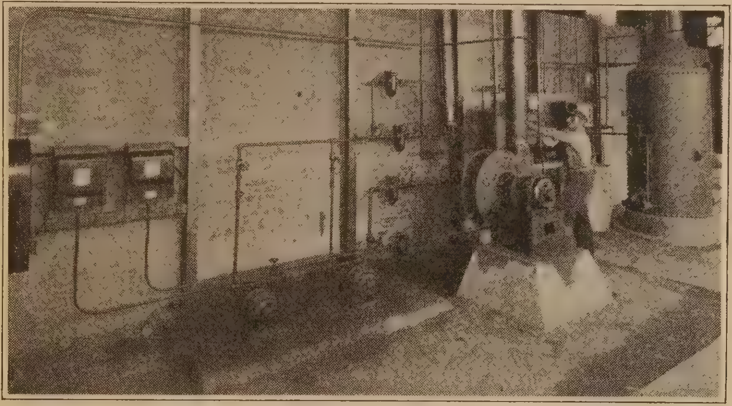

FIG. 2.—This shows the fan, which furnishes the secondary burner air. It also shows the details of the oil pumping system.

It must be clearly understood that the paramount problem in tunnel kiln firing is speed. The total firing time is cut to less than half that required by the periodic kilns. In the case described the best previous periodic kiln record of 96 hours[1] is reduced to 43 hours in the tunnel kiln. Less time is had to deal with the ware and therefore it must be dealt with promptly and properly. The ware begins to cool when it is past the last furnace. No further vitrifying takes place; there is no soaking of heat into the ware at maturing temperature other than that which it gets while in the furnace section. If properly done this is sufficient. In order to obtain greatest capacity through the furnace zone there are three requisites in the direct-fired

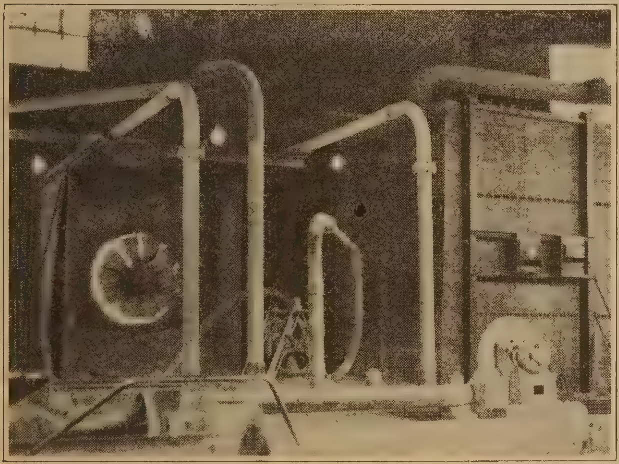

FIG. 3.—Cleaning apparatus at end of tunnel kiln. The coal ashes which have deposited on the face of the settings are brushed off by means of brooms and jets of air just as soon as the cars come from the kiln. Note the exhaust fan, which carries the coal ash to the atmosphere.

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[1] Total time from lighting fires to drawing ware.

tunnel kiln. It is assumed that all combustion has taken place in the furnaces[1].

To get the heat from the furnaces evenly distributed over the cross-section of the car setting requires: (1) volume, (2) velocity, and (3) direction. We must have enough heat, we must have "kick" enough behind it to carry it where we want it, and we must control it so as to put it there, and have it with sufficient energy and under control to put it where it is wanted. If concerned only with a small tonnage, these three requisites would not be of so much importance, but where maximum tonnage delivery is a necessity each of these conditions must be observed carefully. This is the reason that gas and oil make ideal tunnel kiln fuels. They permit of the maximum tonnage in fired ware. Hand-stoked coal is used successfully, but with hand-stoked coal the tonnage of fired ware cannot be as large as when gas or oil is used, unless the ware is highly refractory or close firing is not of primary importance.

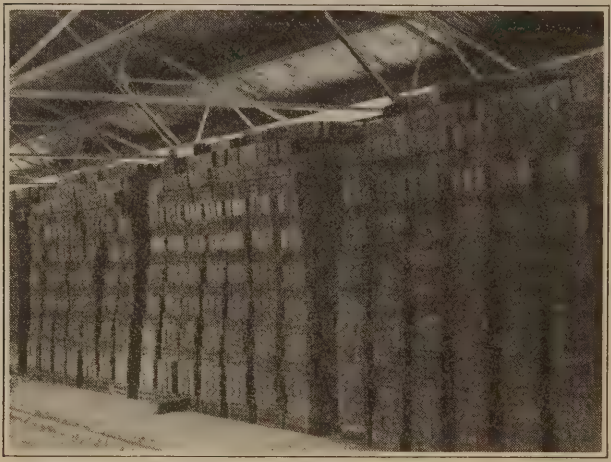

FIG. 4.—Close-up of cars of brick fired with powdered coal. Note at the flues between the brick piers the ashes which have not yet been brushed off. The small amount of ash which remains on the brick is knocked off while handling the brick from the kiln cars to the auto trucks. The ash is not fused to the surface but brushes off easily.

Pulverized Coal Kiln

In the kiln here described, vitrified red shale common brick are fired. Coal, hand-stoked, was first used with success, but the maximum tonnage of No. 1 ware secured could not equal the tonnage in No. 1 ware obtained with oil. With oil, the kiln was put on a schedule of 30 cars per day of properly fired brick. Each car carries over 2,000 brick; therefore, this kiln was producing, when firing oil, over 60,000 brick per day, seven days per week, or a machine production of over 70,000 brick per working day.

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[1] This is not always the case, although nine out of ten kilns are operated with all or almost all the furnaces so regulated that combustion is complete before the gases reach the ware. The tenth kiln may be firing a ware which requires long flames or conditions are such that long flames are desirable, but in most cases short flames are used and the flames are kept entirely out of the tunnel so that when looking down to the furnace section from the discharging end the appearance of the fire zone is absolutely clear like an electric furnace.

After running more than a year on fuel oil, it was decided, due to the uncertain price of oil, to experiment with pulverized coal. Many schemes had to be investigated, their merits determined, and their shortcomings eliminated. Finally after several months of investigation it was decided to use a unit system in which there would be no storage of the coal after pulverization, but where the coal is fired as fast as it is pulverized. No such system had been devised which would pulverize and deliver simultaneously an equal amount of coal to each of ten separate furnaces.

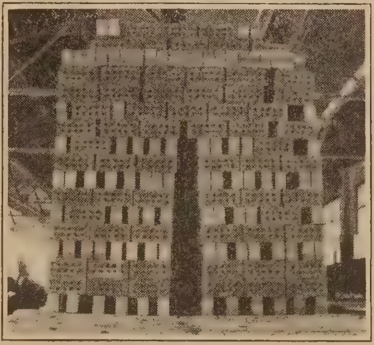

Fig. 5.—This is a close-up of an end of a car fired with powdered coal. Note especially the clean surface of the brick.

Powdered coal will loaf in a line and deposit wherever an opportunity affords. Once it starts to deposit, it builds up rapidly and soon chokes the pipe through which it is flowing. It does not act like a fluid, but must at all times be floated in a stream of air. When powdered coal is stored in a bin the air surrounding the particles soon passes off and the coal packs so that it will not feed steadily through an opening even though it be agitated by a feeding device. It is apparent, therefore, that the amount of coal being fed into the kiln must be closely regulated while the coal is still in slack form before being pulverized.

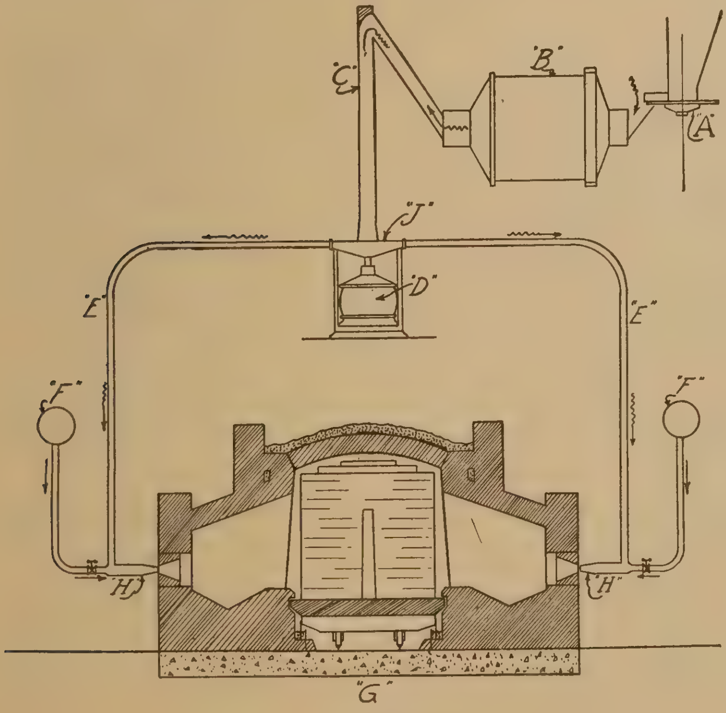

Fig. 6.—Elevation.

The problem was, first, to measure continuously the slack coal, and so regulate this measuring as to control the kiln temperatures; second, to pulverize the coal after being measured, and mix it with air required to carry it to the burners, and third, to divide the stream of coal and air from the pulverizing machine into ten equal parts and a part carried to each of the ten furnaces.

At the furnaces, further furnace temperature control must be had by means of secondary air.

Method and Equipment (See Figs. 6, 7, and 8.) The slack coal is fed from the slack coal bin over disk feeder "A." This disk feeder is of the offset type with a 30-inch table feeding directly into the ball mill "B," which contains 1800 lbs. of 1½-inch forged steel balls and revolves at 31 r.p.m. consuming approximately 20 h.p. This ball mill is about 4 feet in diameter by 5 feet in length, interior dimensions.

An air current is caused to pass through the ball mill by means of the distributing fan "J," the air entering the charging end of the ball mill along with the slack coal, passing through pipe "C" into the inlet of fan "J," fan "J" being driven by a variable speed slip ring motor "D."

After the coal is ground to the required fineness, the stream of air picks up the finely ground coal, carrying it into the distributing fan "J," where the air and coal stream is divided into ten equal parts each of the ten parts going to its respective furnace through pipe "E," as indicated on Fig. 7.

It takes 40 cubic feet of air to transport one pound of coal when pulverized and this mixture of coal and air must travel at a greater speed than 2000 feet per minute in order to prevent clogging of feed lines. Since it can safely be assumed that it takes 150 cubic feet of air to burn a pound of coal, the coal is being transported by 27 to 30% of the air required for complete combustion. This provides a non-explosive mixture in the pipe lines in which the coal is conveyed from the ball mill to the burners.

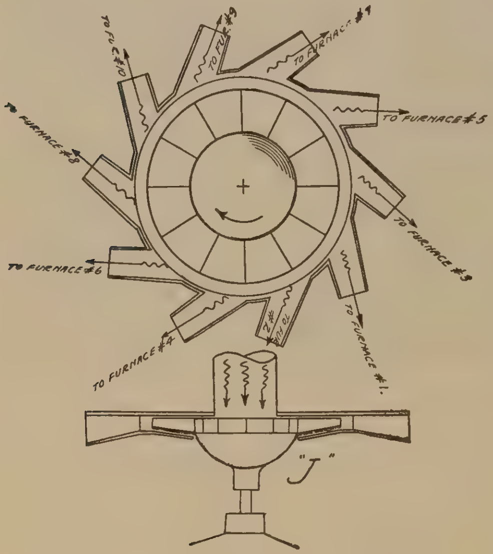

FIG. 7.—Distributing fan detail.

The screen analysis of the powdered coal coming from the ball mill is 53% through 200-mesh, 89% through 100-mesh and all through 30-mesh.

At the burner "H" the vertical descending stream of coal and air enters the rear of the burner and is met by a horizontal stream of air supplied through pipe "F" from an air-supply fan. This gives very good mixing in burner "H" and throws the generated heat from the furnaces into the heart of the setting. Exceptionally short flames have been obtained with this system; in fact, so short as to be considered impossible in the usual powdered coal burning practice. Combustion is absolutely complete within the furnaces and this combustion all takes place within a distance of 5½ feet from the tip of the burner.

Sufficient secondary burner air is mixed with the coal and air stream at the burner to control the combustion in each furnace. Thus, even though the same amount of coal is fed to each furnace, individual furnace control can be secured by means of excess secondary air, thereby diluting the heat generated in the furnace.

The same tonnage of ware is put through the fire zone when burning powdered coal as when burning oil. The results are so satisfactory that this kiln has been operating since September, 1925, on powdered coal. It is possible to change from powdered coal to oil or back from oil to coal in 20 minutes. This is desirable in case of changes or repairs in any of the coal equipment.

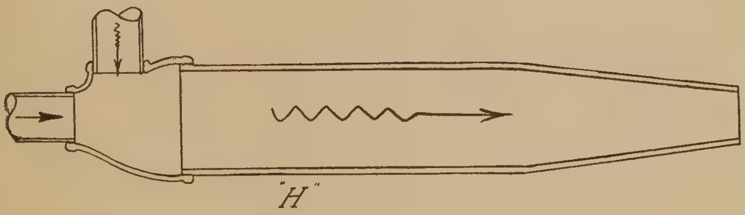

FIG. 8.—Burner detail

When burning powdered coal, 136 pounds of coal are used to fire a ton of brick or 288 pounds of coal per 1000 brick. The coal used is a Hocking Valley coal, from Cambridge, Ohio, containing 5% ash, fusing at above 2000°F. Since the kiln is operated at 1900°F, maximum temperature, the ash does not fuse, but deposits on the faces of the brick and is cleaned off after the car comes from the kiln.

The results obtained are shown in the several illustrations.

Immense credit is due the Ohio Clay Company of Cleveland, Ohio, and especially to George W. Denison, for their fortitude and ingenuity during the development of this method of burning powdered coal in a direct-fired tunnel kiln. It has been a pleasure to assist them in this achievement.

Carl B. Harrop Engineers and Constructors
Columbus, Ohio

GLASS WOOL AS INSULATOR FOR REFRIGERATION PURPOSES[1]

By H. C. Bates

ABSTRACT

A new method has been used to measure the thermal conductivities of insulating materials which consists of the observation of the rate of melting of ice in a vessel insulated with the material under investigation. This is done by noting the change of volume of the mixture of ice and water by means of a graduated glass tube connected to the vessel. Results are given for glass wool of various densities, powdered cork, magnesia asbestos composition, slag wool, Sil-O-Cel powder, cotton waste and sheep's wool. It is also shown that glass wool that can be kept dry is a very superior insulating material.

Glass wool has a number of properties which should make it desirable as a heat insulator. It is light, is proof against fire and dampness, chemicals, rodents, etc., will stand high temperatures, will not decay or deteriorate with use and has low specific heat. It was to be expected that its thermal conductivity would be low and, since this property has not been compared to the conductivity of other materials under identical conditions at temperatures low enough for refrigeration purposes, this investigation was undertaken. Some work has been done in Europe by Hamester and Knoblauch comparing the insulating properties of glass wool with that of asbestos magnesia mixtures, diatomaceous earth, and cork at temperatures higher than atmospheric, and they have shown that glass wool is superior to any of these materials. We have compared glass wool with powdered cork, magnesia asbestos composition, slag wool, Sil-O-Cel powder, cotton waste, and sheep's wool.

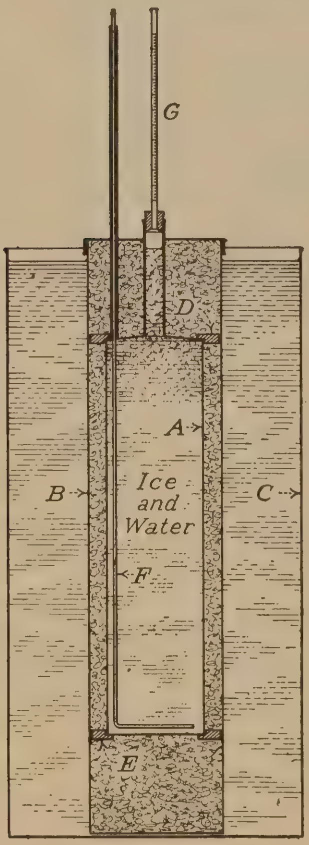

Fig. 1.

The method employed consisted in determining the rate at which ice melted in a container insulated with the various materials. The apparatus used (Fig. 1) was made up of three concentric cylinders, *A*, *B*, and *C*. The inner cylinder, *A*, was of copper and was provided with a long neck into which could be fitted the graduated tube *G*. The other cylinders, *B* and *C*, were of galvanized iron. *A* was held centrally in *B* by means of two annular transite rings,

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[1] Communicated by J. T. Littleton, Jr., at Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Glass Division.) Received June 22, 1926.

D and *E*. The material to be tested was placed in the space between *A* and *B*. The inner can, *A*, was filled with ice and water. The graduated tube was fitted into the neck and water added to bring the level into the tube. The space between *B* and *C* was filled with water. As the heat was transferred through the insulating material ice in *A* was melted and the quantity was determined by the fall of the level of water in *G*. The water in *C* was stirred constantly and the temperature remained constant to one tenth of one degree. The temperature of the ice and water was taken as zero as the mixture was thoroughly stirred by means of rod *F*. The end-losses were reduced by providing six inches of packing at each end of the inner cylinder, *A*. The coefficient of conductivity was determined from the equation:

$$K=\frac{Q}{t(T_1-T_2)\times \text{shape factor}}$$

Where Q is the quantity of heat transferred in time, t, sec. where the difference of temperature between the surfaces is (T_1-T_2) degrees. The value of the shape factor is obtained from the expression:

$$2\pi\left(\frac{L_1}{\log_e \frac{r_2}{r_1}}+\frac{r_1^2+r_2^2}{L_2-L_1}\right)$$

in which L_1 and L_2 are the lengths, and r_1 and r_2 the radii of the inner and outer cylinders respectively.

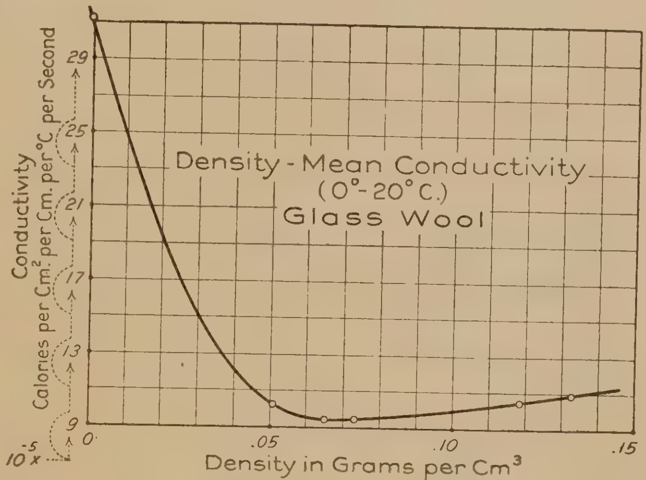

FIG. 2.

The results are contained in Table I. Values obtained by other experimenters are given for comparison.

The values in the table show that glass wool compares favorably with the best insulators available for refrigeration purposes. The curve gives the relation between conductivity and density of glass wool and shows that the most effective packing is that of density equal to 0.065 grs. per cc. The fact that the value is higher for refrigeration than for ordinary temperatures suggested that condensation from the atmosphere might be responsible. To investigate this point a test was made using glass wool which was thoroughly dried by circulating warm dry air through it for ten to twelve hours. The values of conductivity obtained in this way were in agreement with the results

TABLE I

Material	Density grs/cm^3	K(obs.) C.G.S.U.	K (tables)	Remarks
Glass wool	0.133	10.9×10^{-5}		
	0.119	10.5		
	0.073	9.5	7.5×10^{-5}	Hamester's Report
	0.065	9.4		−20°C
	0.051	10.2		
	0.000	31.2		Air only (with convection)
Cork (powdered)	0.140	11.4	10.4	N.P.L. (granulated)
			11.2	N.P.L. (slab)
			10.6	Corkboard (pure) d=0.180
Magnesia asbestos composition	0.340	16.0	15.0	N.P.L.–20°C
			16.0	Randolph–100°C d=0.216
Slag wool	0.247	10.8	10.4	N.P.L.–0°C d=0.208
Sil-O-Cel (powder)	0.147	12.5	12.0	Extrapolated from curve (Celite Products Co.) d=0.22
Cotton waste	0.128	13.3	13.1	Nusselt–0°C
Wool (sheep's)	0.073	8.4	8.4	Firmly packed
			9.2	Nusselt–0°C
			8.5	Randolph d=0.054 at 100°C

quoted in Hamester's report. For very carefully dried samples a value of 6.8×10^{-5} C.G.S.U. was obtained. For dry air free from convection a value of 5.66×10^{-5} C.G.S.U. is given by the Smithsonian Tables at 0°C so that it is evident that dry glass wool provides extremely good heat insulation.

CORNING GLASS WORKS LABORATORY
CORNING, N. Y.

GAS PRODUCES BETTER RESULTS AT LESS COST

By George D. Wilkinson

ABSTRACT

A comparison of gas- and coal-fired sheet iron enamel furnaces is presented. Automatic control is possible with gas with lower amount of discount ware, fewer furnace repairs, increased production capacity, and lower operating cost. Operating cost data are given.

Gas was first tried as a fuel in one of our enameling furnaces about seven years ago. At the present time we operate for wet enamel firing a 4 x 10 ft. semi-muffle type and a 5 x 12 ft. full-muffle furnace. The contract for a third gas-fired furnace, 5 x 12 ft., has been placed and the installation will be made shortly. [This is installed and operating.] The fact that we are still operating two 4 x 10 ft. coal-burning furnaces enables us to offer a direct comparison between the costs and results obtained from the two types of fuel. We are also firing with gas in five 48 x 48-inch semi-muffle dry enamel furnaces, in core ovens, in japaning ovens, and in the smelter.

We manufacture "Universal" and "Home" stoves, ranges, and heaters. Most of the work handled in the enameling department is 18-, 20-, and 22-gage Armco sheet iron, although some of the parts are cast iron. All the work is given three coats. The ground coat is fired at 1650°F and the finish coats at 1580°F. The furnace temperatures are controlled automatically. The 5 x 12 ft. gas furnace is used on ground coats, and the 4 x 10 ft. furnace handles the finish coats.

Surface Combustion Company burners are used in all the gas-fired furnaces, and we find that these burners save approximately 20% of the fuel required by the low pressure burners formerly used. Two motor-driven compressor-units supply gas at 10 lbs. pressure to all the furnaces.

The principal advantage of the gas-fired furnace is the accuracy of the temperature obtained. The automatic control keeps the heat at the proper degree, and after the enameler has set this control for the right temperature no further attention is necessary. The men merely have to watch the time of firing. They need not concern themselves with the temperature.

With coal-fired furnaces the accuracy of the temperature maintained depends upon the skill of the fireman, and while it is possible to secure good results, it is always necessary to contend with the human factor.

Discount Reduced As a result of the more accurate temperature control the gas-fired furnaces reduce the amount of discount very appreciably; in fact, a coal furnace often produces in a single day as much warped, twisted, and defective ware as does a gas furnace in several months. The reduction of discount is the most valuable result obtained from the use of gas in our enameling furnaces, and the saving from this source alone, while not definitely measurable, is obviously great enough to justify the change from coal to gas.

Another important advantage of the gas-fired furnace lies in the fact that they are laid up for repairs fewer days per year than the coal-fired furnaces. In an average year one of our coal furnaces loses about 30 days' production because of repairs, but the gas furnaces lose only approximately 15 days' time. These figures include the time lost while the furnace is cooling to the point where work can be done upon it. This usually amounts to three or four days. After a repair has been made the gas furnace can be brought up to firing temperature in 8 or ten hours, whereas the coal furnace requires about 48 hours.

Productive Capacity Increased 6.4%

The 15 extra operating days obtained each year with the gas furnace are equivalent to a possible increased production of 6.4% compared with the coal furnace.

Of course, gas is cleaner than coal, and it involves no handling expense. When using coal we have to charge to the furnaces the time of one man 24 hours per day for hauling coal, firing, and removing ashes. On Sundays about half of the fireman's time is required to bring the coal furnace up to the temperature required on Monday.

Gas provides a more flexible heat than coal and the temperature can be changed to any desired point very quickly. The gas furnace also has the advantage of maintaining a very even heat throughout the entire furnace.

Lower Operating Cost with Gas

In spite of its many advantages over coal, our records prove that gas is actually cheaper to use. As shown in the attached tabulation the cost of operating the 4 x 10 ft. gas furnace (exclusive of supervision and general overhead) is $77.41 a day of 22 hours. This includes fixed expenses on the furnace and gas compressor, maintenance and repairs, furnace labor, gas, and power for the compressor. The average cost per square foot of single coat fired is $.0088.

The attached tabulation also shows the cost of operating the 4 x 10 ft. coal-fired furnace. This amounts to $79.76 a day of 22 hours. All items except supervision and general overhead are included in this cost which make it parallel to the gas-fired cost given above. Since the daily production of both types of furnace is the same, the cost per square foot of single-coat ware is $.0091.

The 4 x 10 ft. gas furnace, therefore, actually saves $2.35 per day or $587.50 annually in operating cost. The fact that the many advantages of gas, particularly the reduction of discount, can be obtained without additional operating cost, amply justifies our move in changing from coal to gas. Gas has proved very satisfactory in every application we have made to date.

1. Cost of Operation—4x10 foot Gas-Fired Furnace

Depreciation, $4,700.00 ÷ 4 years' life		$1,175.00
[1]Average interest at 6%— $\frac{5}{4}\times\frac{\$4{,}700.00\times .05}{2}$		176.25
Depreciation and interest on 2 gas compressor units:		
Depreciation, $2,200.00 ÷ 4 yrs.	$550.00	
[1]Average interest at 6%— $\frac{5}{4}\times\frac{\$2{,}200.00\times .06}{2}$	82.50	
	$632.50	
Amount chargeable to one furnace— $632.50 × 25%		158.12
Annual allowance for all maintenance and repairs, including rebuilding side tiles every 1½ yrs., maintenance of burners, piers, etc.		250.00
Total fixed expense, per year		$1,759.37
Fixed expense, per day—$1,759.37 ÷ 250 days		$ 7.04
Furnace labor, 22 hrs. at $2.50 (3 men, average)		55.00
Gas, 26,400 cu. ft. at $.52 per M.		13.73
Power for driving compressor (proportion chargeable to one furnace), 82 kw.-hr. at $.02		1.64
Total cost per day (22 hours)		$ 77.41
Average production per day (22 hours)—8,800 sq. ft. (single cost)		
Firing cost per sq. ft. of single coat, $77.41 ÷ 8,800		$ .0088

[1] Allowing for interest earned by depreciation reserve.

2. Cost of Operation, 4x10 foot Coal-Fired Furnace

Depreciation, $5,000.00 ÷ 4 years' life	$1,250.00
[1]Average interest at 6%— $\frac{5}{4}\times\frac{\$5{,}000.00\times .06}{2}$	187.50
Fixed expenses on stack (proportion chargeable to one furnace)	59.85
Annual allowance for maintenance and repairs	500.00
Total fixed expense per year	$1,997.35
Fixed expense, per day, $1,997.35 ÷ 235 days	$ 8.50
Furnace labor—22 hrs. a $2.50 (3 men, average)	55.00
one fireman—24 hrs. a $.50 = $12.00 ÷ 2 furnaces	6.00
Sunday firing cost, prorated over operating days	.50
Coal, 1.5 tons a $4.24	6.36

[1] Allowing for interest earned by depreciation reserve

Rent on space for coal storage, $800.00÷235 days		3.40
Total cost per day (22 hours)	$	79.76
Average production per day (22 hours), 8,800 sq. ft. (single cost)		
Firing cost per sq. ft. of single coat, $79.76÷8,800	$	.0091

Saving Effected by Gas Furnace

Cost per day, coal-fired furnace	$	79.76
Cost per day, gas-fired furnace		77.41
Net saving, per day	$	2.35
[1]Net saving, per year, $2.35×250 days	$	587.50

[1] Does not include savings due to reduction of discount, etc.

Cribben and Sexton Company
Chicago, Illinois

MODELED TREATMENT OF POTTERY[1]

By Marion Lawrence Fosdick

ABSTRACT

This paper is intended as one of a series on processes of decoration of pottery, and is a discussion of modeled treatment, where and how it is successful decoratively and from the point of view of practicality. The process of modeling with coils in low relief is given in detail. Vigorous pattern is used if the glazes are to be matt because of the thicker nature of the glaze which will obliterate subtlety in the modeling. Delicate pattern is used under thinner and more fluid glazes. Formulas are given for one series of vivid colors of a matt glaze and for a treatment of transparent, rather neutral glazes, on a clay red-orange in color.

Modeled treatment may be as fundamental as slip painting. There is a need for it, which is the first requirement for any pattern. Slip painting may be used when change of color is desired, or variety of values in color. Modeled pattern creates by its third dimension a pattern of light and shadow. This may give any number of values, according to the number of heights of the modeling. Its worth lies in the very gentle change of values thus brought about, which is more desirable on some surfaces than change of color. It also changes texture very charmingly, adding high lights in the case of a brilliant glaze which make a sparkling surface, lovely with high keyed colors or those toward white.

Modeling on pottery, therefore, is of use where it is desirable to have the surface patterned without change of color. The modeling may be bold and vigorous or so delicate that it is a tracery, or cobweb pattern, thrown across the surface. Its virility or its delicacy, one or the other, has three causes. First, the detail of the pattern may be strong or delicate. Second, by the height of the modeling from the background deep shadow or very light shadow may be produced. Third, by the gradual or steep slant of the part modeled on, depth of shadow or lightness may be accentuated.

Modeled Pottery Must Be Part of Object

One thing should be emphasized thoroughly in this treatment. The modeled pattern must be in effect a part of the object. It must have no suspicion of being applied. It must first be used only where surface treatment is needed and when used must seem to have grown from the clay and not in any case to be lying on the clay as an appliqué. It can be an exquisite treatment if it is so used as to seem an outgrowth from the clay and still be a part of the clay body.

The Chinese were delightful in their understanding of this mode of decoration and treated it imaginatively as well as with due regard to its technical requirements. In the Garland Collection (later a part of the Morgan Collection) are some of their loveliest examples of treatment of clay in releif, both vigorous and delicate. In their more vigorous treatment it is used as a frame (in low relief but bold in character) about piercing. In this delicate treatment it stresses lightly some part of the construction of the vase or forms the surface tracery pattern which was mentioned earlier. In all cases it is so used that it is necessary to the beauty of the vase, is never obtrusive and is in character with the vase, that is, subtle or strong according to the contour of the piece of pottery and the use for which it is intended.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Art Division.)

Clay Must Be Soft for Welding

As to the process of modeling in relief the technical requirement is of a surface soft enough to receive clay and clay soft enough to be welded quickly and with little pressure. Tiny coils, laid on lightly and welded with a thin tool or the fingers, will keep the first spontaneous line of the pattern. It is hardly necessary to tell experienced potters that a vase built and already stiffened does not take fresh clay safely. Cracks are a natural result when fresh clay meets older clay which has already undergone air shrinkage.

The writer finds it very satisfactory to finish one part before starting another, in contrast to laying out the entire pattern in clay coils before finishing perfectly each part. Spontaneity is desirable and the surface of the modeled pattern has more freshness and more of the charm coming from that, if it is finished before the clay stiffens. For that reason, in the case of a large plate for instance, where the design calls for pattern in the center, or a surface pattern, it is more satisfactory to model the pattern as soon as the center of the plate has been built and before building the sides. This also insures safe welding of the tiny coils of the pattern—before the center of the plate has stiffened. Of course, work in sections requires an extremely clear, satisfactory design from which the potter works in order to insure beauty of the whole.

Height of Pattern Must Be Even

Whether in high or low relief, if the height of the modeled pattern from the background is even throughout, a fine pattern of three values is insured. This is important because poise is acquired in decorative work through the keeping of values clearly and with precision. This is in contrast to relief in sculpture. By varying heights of the pattern more values are produced and depth of interest may be gained by using two or more heights of relief, thus adding one or more values. But it should always be remembered that too great height in relation to the size of the vase creates the feeling of an appliqué and destroys the very result worked for.

Fluidity of Glaze Important Color and kinds of glazes are so important in modeled pattern that they should be considered from the first. Except in bolder work there is very sensitive feeling in modeled pattern when it is successfully done. Neither a glaze which has to be thickly applied (as a matt glaze) nor a very fluid glaze is as successful as a glaze with the average content of an alumina, one which is fine in color texture if thinly applied. The writer associates deep, vibrant colors or those vivid and high keyed with the bolder, more direct modeled pattern, and with the delicate variety, paler colors, whether high keyed or neutral. A pale crackled glaze may be very lovely when used for delicate modeling, not only because of its color but because of its thinness. With a certain degree of fluidity, it draws off the modeling enough to intensify whatever subtlety may be in the modeling.

Suggested Glazes

In suggesting one or two color schemes, and offering certain formulas the writer recognizes that a wonderful variety of combinations of clay and glaze has not been touched by her. These given have seemed successful and worthy of study. In her classes, the colors have been discussed and the pottery designed with its color and its ultimate treatment of surface in mind. Miss Clara K. Nelson, Professor of Design at the New York State School of Clayworking and Ceramics, has suggested many treatments in color and worked with the writer on various plans for color still to be executed.

The crackled glaze, containing enough tin oxide to be semi-opaque, is very fine if used over modeled red-orange clay. The Dover Pottery at Hartsdale has beautiful quality in its pottery treated thus, though more of it is plain than modeled. A light green crackled glaze is also fine, and on edges and parts where it is applied very thinly it shows a metallic luster apparently due to slight overcharging with the copper oxide. In the colorless crackle, however, the flush of the red-orange clay through the glaze is exceedingly lovely. A clay body made of 4 parts of Enfield red clay 2 to 1 part of Campbell's red is satisfactory.

Another combination with interesting possibilities is that of a deep red-orange clay modeled and glazed very thinly with a transparent glaze colored with 0.25 of a gram of cobalt oxide to 320 grams of glaze. This is very lightly sprayed after it is dry with a pale violet enamel, colored with manganese carbonate, 4 grams. The result is a vibration of violet over red-orange, somewhat neutral in color but alive.

Modeled pattern has fine possibilities for inlaying if one uses the pattern as a means of holding pools of glaze of different colors. Color schemes successful in sturdy objects such as coffee jug and cups were of four glazes, orange, yellow, blue, and green. The blue, yellow, and green were like in value. They were made of the barium matt glaze, maturing at cone 04, with the following amounts of color added to the batch of 321 grams of this glaze:

Blue—cobalt oxide	0.5 grams
Green—copper oxide	4.0 grams
Yellow—yellow base	10.0 grams

The orange was the orange matt glaze originated at the New York State School of Clayworking and Ceramics, the formula of which follows:

Frit	red lead	228.0
	flint	96.0
	uranium oxide	75.0
	Canadian feldspar	56.0
Glaze	frit	168.0
	whiting	20.0
	barium carbonate	40.0
	calcined clay	32.0
	white lead	50.0

Of course the glazes used must mature at the same temperature, otherwise one will be immature and rough when another has fused.

As to the application of these glazes, the pottery was dipped and lightly sprayed and from then on was kept in the damp box. Water was sprayed on it if during the inlaying the coat of glaze became too dry. The background spaces were first cut around, then scraped away with a small knife, and the desired color was then painted on with a brush. Dampness of the pottery is desirable because in this way one can cut a clear line in the glaze and also in order that the clay may not suck up too quickly the glazes applied with the brush. It is a treatment where imperfection means crawling and like all other ceramic work requires materials and implements in right condition.

All of this will seem of little moment perhaps or of too much detail to the potter who feels instinctively his clay. The other type of potter, however, works his way to technical freedom step by step by working from one fine point to another. Each seems to work miracles which are, however, only patient control of an exacting medium.

New York State School of Clayworking and Ceramics
Alfred, N. Y.

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ORIGINAL PAPERS

CHARACTERISTICS OF PYROMETRIC CONES[1]

By C. O. Fairchild[2] and M. F. Peters[3]

ABSTRACT

For the first time the characteristics of pyrometer cones have been determined under definite and reproducible conditions of heating. The temperatures of the "end points" of a complete set of cones together with their bending intervals were measured at carefully controlled rates of heating in clean air and in various kiln gases. Heated at 20°C per hour in furnace gases free from SO_2, the end points of cones 015 to 01 are somewhat higher than those observed when the cones were heated in clean air. Cones 022 to 016 and 1 to 42 were acted upon only slightly by kiln gases free from SO_2. There is more significance in the demonstration of the utility of measuring the end points of the cones under accurately controlled and known conditions of heating than in the numerical results obtained.

Introduction

Pyrometric cones are the most widely used of all devices for the control of the heat treatment of clay products and therefore engage the interest of all ceramists. The fullest usefulness of these devices depends primarily upon reproducible quantitative data obtained under standardized conditions approximating those met with in ceramic practice. To procure such data was the aim of the investigation here described.

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[1] Published with permission of the Director, Bureau of Standards, Department of Commerce. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. Revised and received by Editor, July 24, 1926.

[2] Physicist, Chief of Pyrometry Section.

[3] Associate Physicist, Pyrometry Section.

A few years ago some of us believed that pyrometers would ultimately displace cones for the control of kilns. This position was taken not without reason but without a sufficient appreciation of the problems in ceramic firing.

The advice of successful ceramists has for years been and still is to use pyrometers not occasionally but constantly. in every kiln and fire, but unless the behavior of a cone in a kiln can be fairly accurately associated with temperature it will be very difficult to correlate its behavior with the indications of a pyrometer and consequently it will be impossible to make full use of both.

A committee of ceramists was asked to coöperate and advise concerning ceramic practice in its relation to the use of cones. This Committee consisted of P. H. Bates, Chairman, representing the AMERICAN CERAMIC SOCIETY; Edward Orton, Jr., proprietor of the Standard Pyrometric Cone Co.; James Turner, representing the United States Potters Association; Walter S. Mayer, vice president, Mayer China Co., and manufacturer of "Mayer" cones; M. C. Booze, representing the Refractories Manufacturers Association; and R. F. Geller, representing the Ceramic Division of the Bureau.

The Committee met on May 5, 1924, and made recommendations concerning rates of firing and methods of mounting cones. The method of studying the effects of kiln atmosphere was approved. The Committee advised limiting the present studies to cones made by the Standard Pyrometric Cone Company.

This investigation was directed to accomplish the following:

1. Accurate determinations of the "end points" of cones, and the influence of firing rate and furnace atmosphere upon them.
2. Establishment of standard methods for testing cones, thereby indicating methods for testing the refractoriness of materials.
3. Development of laboratory methods which will produce results applicable to plant conditions and industrial practice.
4. Promotion of the practice of pyrometry in ceramic engineering.
5. Decision as to whether cones should be used in laboratory tests of clay products.

Historical Review

Credit for the invention of the fusible cone has been given to Lauth and Voght,[1] but their invention was apparently not followed by widespread industrial use. In 1886, Seger published[2] the descriptions and compositions of cones 1 to 36, making no reference to the work of Lauth and Voght, and industrial application immediately followed.

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[1] *Bull. Soc. Chim.*, **46**, p. 786 (1886); cf. Burgess and Le Chatelier, "High Temperature Measurements," p. 368, 1912.

[2] Collected Writings, I, p. 224. Gesammelte Schriften, p. 178.

Pyrometry was in its infancy in 1886 and there was no satisfactory means for measuring kiln temperatures at that time. This condition was recognized by Seger and he proceeded in an endeavor to invent a reliable pyrometric device. His purpose is set forth in the following quotation:

> If now, in order to follow a proposition made by Dr. Heintz of Saarau, we disregard the determination of temperatures according to the ordinary conception of degrees, for the purposes of the ceramic industries, we can put in its place a series of tetrahedrons made out of glazes which melt down, one after the other, and infer the temperature attained from the number of tetrahedrons which have melted or express the attainment of a certain temperature in the kiln by the melting of a definite glaze.

While it may appear from this quotation that Seger proposed to set up a temperature scale expressed in "cone numbers" for use exclusively in the ceramic industries it is evident that he believed each cone possessed a definite melting point and that each cone number corresponded to a definite temperature. Believing this to be the case, he wrote as follows:

> I am of the opinion that a scale of refractoriness for the testing of fire clays alone is not good in principle, but that one scale should be made applicable to all industries; for if every industry will adopt its own scale for the measurement of temperatures others will naturally be led to measure fire clays with their standards, and great confusion and errors would be the result.

The original cone-temperature table was published about 1900. This table included cones from 01 to 022 devised by Cramer and Hecht.[1] It was soon learned[2] that the cones when used in large, slow heating kilns fused at lower temperatures than those given in the table.

The effect of furnace gases upon the "end points" was not generally noticed, although, in 1900, Gorton[3] described the action of kiln gases upon cones containing iron oxide.

Ceramists were at this time inclined toward overconfidence in the temperatures indicated by pyrometers, although experimenters in other fields were finding that pyrometer errors were of the same magnitude as the differences apparent between cones and pyrometers. Geijsbeek[4] criticized Orton[5] and Purdy[6] for doubting the accuracy of their temperature measurements, but only a few years previously the temperature scale had been changed about 15° at 1100°C.

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[1] *Tonind. Zeit.*, 1892, 1895.

[2] *Trans. Amer. Ceram. Soc.*, **1**, 23 (1899).

[3] *Ibid.*, **2**, 60 (1900).

[4] *Ibid.*, **6**, 94 (1904).

[5] *Ibid.*, **5**, 305 (1903).

[6] *Ibid.*, **5**, 160 (1903).

Purdy,[1] in studying the behavior of stoneware glazes fired on a time-temperature schedule "as closely as possible, using a thermocouple pyrometer" and made the significant statement that:

> While these glazes thus tabulated fused considerably under cone 2, and would give good glassy glazes at cone 2 or lower when fired in as short a period of time as this test, they would require cones 5–7 in the longer firings of the regular stoneware operations.

In 1907, Hofmann[2] determined the fusion temperatures of cones 1 to 20 in an iridium tube furnace, heated at a rate of approximately 300°C per hour and open to air. Two years later he extended the investigation to cone 35 by the same method and, in 1911, he published the results of temperature measurements of the "end points" of a few cones heated in industrial kilns. These later tests covered only cones 2 to 17 in a few kilns heated according to the regular schedules, but left no doubt that the cones came down 40 to 100°C below the temperatures observed in the iridium tube furnace. The results were considered merely as indicative of unavoidable differences and no attempt was made to establish the exact conditions under which the cones were heated in the industrial kilns.

Rieke[3] studied cones 022 to 15 including the new "a" series developed by Simonis[4] and concluded: (1) fusion points are dependent on the rate of heating, a most important factor; (2) cones melt at lower temperatures when heated slowly except certain ones which are in a way devitrified especially on the surface; (3) from cone 1 up slow heating lowers the melting points sometimes as much as 100°C; (4) the melting temperatures cannot be determined once for all. Cones can be used for temperature measurements only when the temperatures "have been ascertained for definite, exactly reproducible conditions"; (5) the usefulness of cones depends mainly upon the fact that they consist of silicate mixtures *more or less resembling ceramic compositions and consequently are similarly influenced by varying conditions.* [The italics are ours.]

Geijsbeek[5] published in 1912 a résumé of the previous work and stated conclusions similar to Rieke's.

Orton stated in the discussion of Geijsbeek's paper:

> It is generally conceded that it is unfortunate that Seger in first introducing the cones brought in the idea of using them for measuring temperatures, and there are grounds for believing that Dr. Seger recognized this himself shortly after it had been done.

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[1] *Trans. Amer. Ceram. Soc.* **1,** 23 (1899).

[2] *Tonind. Zeit.,* **31,** 1366 (1907).

[3] *Sprechsaal,* **44,** 726 (1911).

[4] *Ibid.,***41,** (1908); *Tonind. Zeit.* (1908).

[5] *Trans. Amer. Ceram. Soc.,* **14,** 849 (1912).

Bleininger and Brown,[1] in 1911, while discussing the viscosity of clays at high temperatures, wrote:

> The saving feature of the Seger cones is the fact that, ... they are (always) subject to practically the same gravitational pull, and hence, bend over as soon as a certain degree of fluidity has been attained.

Sosman[2] appears to be the first to apply the laws of physical chemistry to a study of pyrometric cones. The influence of eutectics and compounds formed during vitrification and fusion, on the behavior of cones, was emphasized by this author. He also pointed out the causes for the slow fusion of cones and agreed with others that this characteristic contributes to their usefulness as "indicators of heat effects and as such they are very efficient tests for the control of an industrial process."

Brown and Murray[3] observed that:

> It is impossible to work out general rules governing the time temperature relations because certain properties of the clays, such as viscosity at kiln temperatures, vary widely.

Stover,[4] in a paper on "Pottery Firing by Pyrometry" recommended the use of all available means for control including pyrometric cones.

In 1918, Fieldner, Hall, and Feild[5] investigated the cone method of testing the fusibility of coal ash. They gave particular attention to the effects of reducing atmospheres upon cones containing iron and gave an extensive bibliography including the physical chemistry of silicates.

The first contribution to studies of silicate reactions at high temperatures by physico-chemical methods is that of Day and Shepherd[6] on "The Lime-Silica Series of Minerals." They point out the failure of the cone method of determining the melting point of a eutectic mixture or a compound.

Day and Sosman[7] who determined the melting points of a great many minerals, wrote as follows concerning melting phenomena:

> The so-called melting interval of slow-melting compounds (quartz, albite, orthoclase) should be carefully distinguished from the "melting interval" of mixtures (lime-soda

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[1] "Testing of Clay Refractories," Bur. of Stand., *Tech. Paper*, No. 7 (1912).

[2] "The Physical Chemistry of Seger Cones," *Trans. Amer. Ceram. Soc.*, **15**, 482 (1913).

[3] "Function of Time in the Vitrification of Clays," *Trans. Amer. Ceram. Soc.*, **15**, 193 (1913).

[4] *Trans. Amer. Ceram. Soc.*, **15**, 364 (1913).

[5] Bur. Mines, *Bull.*, No. 6., 129 (1918).

[6] *Amer. Jour. Sci.*, **27**, 265 (1906).

[7] *Amer. Jour. Sci.*, **31**, 341 (1911).

feldspars, impure natural minerals). The former melt and become amorphous very slowly, but their melting interval is an interval of *time*, whereas the melting interval of mixtures is an interval of *temperature*. The pure soda feldspar (albite), if held at a temperature slightly above its melting point for a sufficient length of time, will melt completely; the mixture, on the other hand, if held at a temperature within its melting interval, will melt in part, come to equilibrium, and remain indefinitely part crystalline and part liquid.

Limitations of Present Work

In the complete series of cones from 022 to 42, sixty in all, the compositions of forty-eight are relatively complex, some of them containing as many as five minerals and a prepared glass. Eleven of the series are made from varying proportions of silica and alumina, and the last cone, No. 42, consists of alumina alone. With the exception of the last-named and No. 35, which is pure kaolin, none of the entire series is intentionally made as a definite chemical compound or a eutectic mixture.

It is apparent, therefore, that the behavior of a cone during its heat treatment depends, in general, upon a complex array of factors very few of which can be separately or definitely evaluated. The principal properties and actions of cones may be determined while the physical and chemical transformations within each cone in a rising fire may properly remain for a later study.

The compositions of all the cones, in terms of the raw materials used by the manufacturer, have been furnished the Bureau of Standards in confidence by the maker. This information has made it possible to account for variations in properties from one cone to the next and to fit the experiments to the composition.

Brief Description of Behavior of Cones and Factors Involved

The factors which control the actions of cones during their heat treatment may be divided into two classes, *viz.*, (*a*) those controllable to a large extent by the maker, and (*b*) those controlled to a greater or less degree by the user. The first class includes (1) size and shape, (2) fineness of particles, (3) intimacy of mixture, (4) porosity and homogeneity, (5) chemical and mineralogical composition including impurities, (6) physico-chemical composition of materials and particles including whether they are crystalline, colloidal, amorphous or glassy, and whether water of crystallization, dissolved or adsorbed gases, etc., are present, and (7) unknown factors controlled by fixed methods of making. Those in the second class are: (1) mounting and position, (2) oxidation of organic binder, (3) release of H_2O and CO_2, (4) rate of firing, (5) furnace atmosphere, (6) unknown factors controlled by standardized practice.

All these factors may be described differently from the point of view of what takes place within the cone during firing, as follows:

(1) drying and shrinkage, (2) loss of combined H_2O, (3) firing of binder, (4) loss of combined CO_2, (5) reactions with surrounding atmosphere, (6) softening of most fusible constituent, (7) partial loss of volatile constituents such as B_2O_3 and alkalis, (8) chemical reactions and molecular rearrangements, (9) solution of solids in liquid, (10) continued shrinkage, bending, and the effects of surface tension and gravity, (11) crystallization from the liquid constituent, (12) final fusion or melting.

Cause of Bending

During the heating of a cone it changes from a porous, heterogeneous, solid material into a viscous or, more properly, a plastic one, never reaching (except during very slow firing) a condition of chemical or physical equilibrium. This change is followed by bending or deformation as the temperature rises. The deformability (plastic or viscous) at any instant is determined not only by the temperature as in the case of a pure simple substance not undergoing molecular changes, but by many changes taking place within the cone, and hence by the length of time elapsing after the cone has reached a certain temperature. It is readily apparent that no simple general law expressing the deformability or consistency as a function of time and temperature can be deduced for cones as can be done for most glasses and many other viscous materials. That there is no general law for fusibility as a function of the content of fluxes was discovered long before "eutectics" were recognized or defined.

However, the maker of cones, by careful trial and control of his manufacturing processes has demonstrated his ability to grade rather uniformly, a series of mineral and chemical mixtures, in such a way that they react in a graded manner to heat treatment. That is, despite the fact that the same eutectic mixture may occur or form in successive cones of a series, care in making them can to some extent mask the influence of the eutectic and produce a truly graded series.

The temperature at which a cone starts to bend may be regarded for some purposes as the temperature at which the viscosity of the glass constitutent has decreased or the amount of glass formed has increased to such an extent that the cone's own weight begins to deform it. The initial deformation may be caused not only by the force of gravity but also by the forces due to shrinkage and vitrification. However, the motion caused by these latter forces is generally slight at temperatures below that at which gravity alone bends the cone. In some cases, to be sure, distortion due to shrinkage may precede what may properly be taken as the true start of bending, and in such cases it is difficult for an observer to decide when bending due to gravity alone commences.

Rate of Bending During the bending, the viscosity depends not only upon the temperature but upon reactions which may occur within the cone. For example, bending may be almost completely halted by a reaction which absorbs or greatly alters the most fusible constituent present. On the other hand the bending may accelerate "abnormally" if the composition of the glass changes. In general, the viscosity decreases and the rate of bending increases if the temperature is rising, but if the temperature remains steady the viscosity normally does not change much. In either case bending will not cease and the cone will finally reach its "end point," which is defined as the temperature at which the tip touches the pat on a level with the base of the cone. This temperature depends, therefore, upon the rate of heating.

Suppose, for example, it is intended to heat the cone at a constant rate. Then at the end of a certain interval of time and at a certain temperature the tip of the cone will reach the pat. If, however, just before this instant the temperature departs from the schedule, the tip will still reach the pat at very nearly the correct time, but the end point will be in error by approximately the departure from the scheduled temperature. If, on the other hand, the rate of heating is changed to a new constant value at a temperature well below the start of bending, the end point will closely approximate the temperature properly assignable to the new rate.

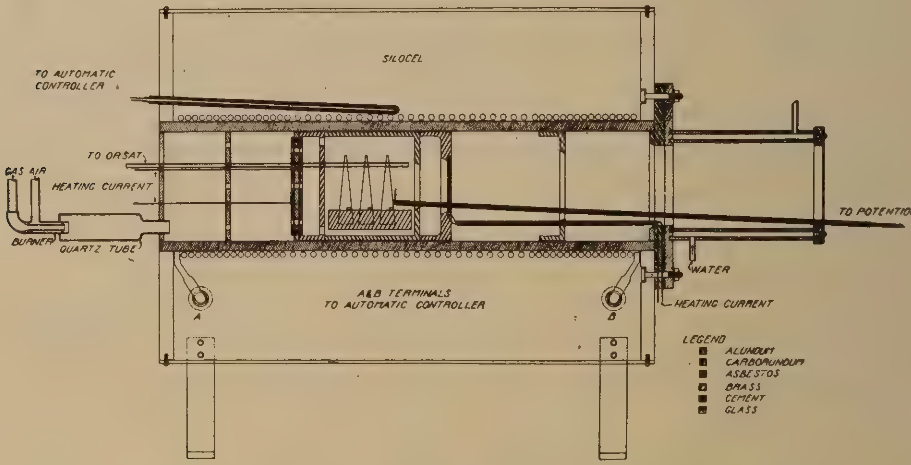

FIG. 1.—Alundum tube furnace with nickel-chromium wire heating-element.

Apparatus and Methods

Furnaces For the experiments with cones fusing below 1200°C, the electric tube furnace shown in longitudinal cross-section in Fig. 1 was constructed. It consists of an alundum tube wound with a heavy (No. 8 gage) nickel-chromium wire heating-element and diaphragmed with partition walls of Carborundum so as to provide an inner chamber which could be uniformly heated. This chamber is placed somewhat toward the rear of the furnace to offset the loss of heat by radiation through the openings which were necessary for observation of the bending cones. Two of the diaphragms are supplied with small wire heating-elements so that axial temperature gradients can easily be adjusted.

It was not necessary to seal the furnace during tests of the performance of cones in air, but in other tests when various gaseous mixtures were introduced, the back was luted with cement and the front was sealed with a water-cooled glass window. In such tests, the products of combustion from a gas flame entered through the rear wall, traversed three chambers before reaching the inner one and escaped through small openings in the front. In this way the gases attained approximately the temperature of the cones before passing over them.

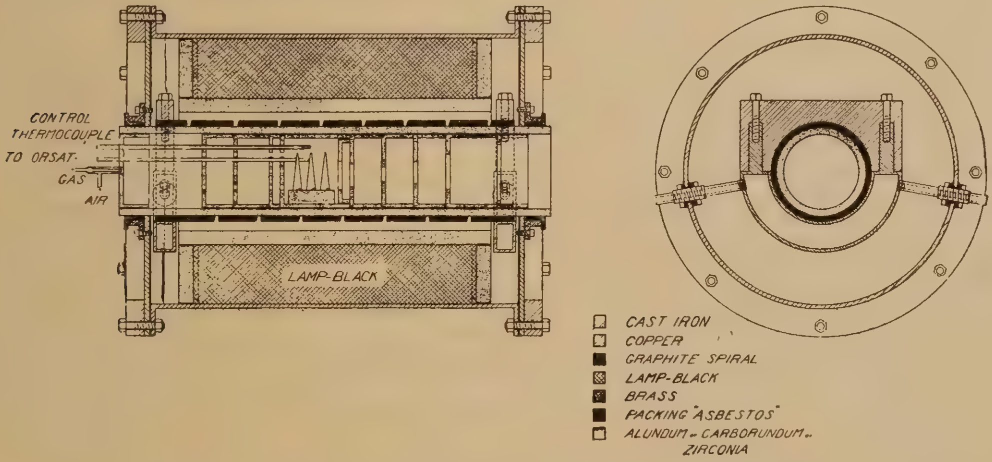

FIG. 2.—Electric furnace with graphite-spiral heater.

The graphite-spiral furnace shown in Fig. 2 was designed to heat the more refractory cones in an oxidizing atmosphere. It consists of a gas-tight iron container holding a graphite spiral between water-cooled copper terminals. A Carborundum tube surrounds the spiral, and within the spiral a tube of Carborundum, alumina, or zirconia[1] is placed, which extends through packing-rings on the end plates. Thus the graphite heater is protected to some extent from the air, and as an additional safeguard against rapid oxidation of the graphite, the space surrounding it is kept filled with illuminating gas. The inner tube is diaphragmed as before, but it was thought impracticable to provide any of the diaphragms with auxiliary heaters capable of withstanding the high temperatures for which the furnace was intended. Therefore, to promote temperature uniformity within the inner chamber and, at the same time, permit a full view of cones mounted in it the diaphragms with a different arrangement of openings, are placed closer together than in the other furnace.

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[1] The inner tube and diaphragms made from materials at hand failed at 1840°C slightly above the end point of cone 38. Carborundum tubes and diaphragms were satisfactory up to 1400°C, at which temperature oxidation of the material proceeds fairly rapidly. Tubes made from a mixture of 40% No. 518 Norton cement with 60% white alundum, ground to 60-mesh failed at 1840°C. The zirconia at hand contained considerable silica and did not prove to be very serviceable. An Arsem furnace of old design which does not require description was employed in the determinations of the end points of cones 39 to 42 after learning its performance in checking cones 34 to 38. See Table VI.

Temperature Measurements Temperature measurements were made in accordance with the practice described in a publication[1] of the Bureau of Standards. Temperatures given in the present paper are consistent with the "melting points"; zinc, 419.4°C; aluminum (99.85% pure), 659.8°C; gold, 1063°C; palladium, 1553°C.

Below 850°C, temperatures were measured with base metal thermocouples made from No. 22 B. & S. gage chromel and alumel wire. These couples were calibrated by comparison with the primary standard rare metal thermocouples of the Bureau of Standards. Between 850 and 1100° either the base metal couples or optical pyrometers of the disappearing-filament type were employed, and higher temperatures were measured only with the latter type of instrument. During some of the measurements the primary standard optical pyrometer of the Bureau or a modified[2] Leeds and Northrup pyrometer was used.

The Leeds and Northrup pyrometer was calibrated by comparison with the primary standard.

To reduce the errors as far as possible the temperature of each cone in the furnace was measured separately. At lower temperatures a thermocouple mounted in a two-holed porcelain insulating tube was inserted through the front window of the furnace, as shown in Fig. 1, and placed so that its hot junction lay close to the cone whose temperature was to be measured. The bare end of the couple extended beyond the end of the insulating tube about three centimeters and was bent into an arc whose plane was at right angles to the tube so that this curved part of the couple could be brought very close to the cone at the moment the latter reached its end point. Thus the hot junction of the couple is very nearly at the same temperature as the cone.

A new, homogeneous couple was used for each run, or heat, and in the absence of any fumes or gases in the furnace, which would rapidly attack the couple, there was little likelihood that it could develop appreciable heterogeneity during the few hours of its use.

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[1] "Pyrometric Practice," *Tech. Paper*, No. 170, Foote, Fairchild, and Harrison.

[2] Fairchild and Hoover, *Jour. Opt. Soc. Amer. and Rev. of Sci. Inst.*, **7**, 543 (1923).

At higher temperatures an optical pyrometer was sighted through the front of the furnace into a small hole drilled in the cone as shown in Figs. 1, 2, and 3. Measurements were necessary to determine the temperature gradient from the base to the tip of the cone.

The relative positions of the cones in the furnace were altered in repeated runs so that in most cases a cone of a given number was tested in each of the three positions shown. By this means, and by measuring as nearly as possible the temperature of each cone separately, errors due to small temperature gradients were, no doubt, almost negligible. It is believed that the accuracy with which the end points of cones fusing below 1400°C was established was better than 5° and at higher temperatures it was better than 10°.

Measurements of the temperatures within the cone chambers of the furnaces served as checks upon the accuracy with which rates of heating, controlled by separate means, were maintained.

Control of Rate of Heating

In Fig. 1 is shown the thermocouple for controlling the heating rate. It is mounted in a porcelain tube placed close to the heating element on the outside of the furnace tube. By watching closely with a sensitive galvanometer the rate of increase of the e. m. f. of this couple while the furnace was heating, a very slight departure from the schedule could be detected and corrected even before it was apparent within the cone chamber. Account was taken of the difference in temperature between the cone chamber and the control couple and the slight change of this difference as the temperature increased.

The graphite-resistor furnace shown in Fig. 2 was controlled with an accuracy almost equal to that attained with the other, although in this case the control couple was farther from the heater. A rare-metal thermocouple was selected for the high temperatures reached with this furnace and proved to be useful, in the position illustrated, up to 1600°. It was withdrawn from this position to a cooler part of the furnace as the temperature rose above this value and, as before, correction was made for the difference in temperature between it and the cone chamber.

During very long runs at a slow rate of heating, the control couples were connected to an automatic temperature controller made by the Leeds and Northrup Company and modified at the Bureau. Automatic control, however, gave a constant average rate fluctuating somewhat with the operation of the device and for this reason hand control was always used through the temperature range in which the cones in the furnace were bending.

Two rates of heating were used, 20°C and 150°C per hour.

Control of Gas Control of the compositions of the gas used was accomplished with relative ease by careful adjustments of the gas-burners and the employment of pressure regulators in the gas and air lines.

The products from the combustion of Washington illuminating gas do not contain an appreciable percentage of sulphur dioxide, so it was necessary, for study of the action of sulphur dioxide upon the behavior of cones, to add it to the products from the gas flame. It was obtained from a cylinder of liquid SO_2 and the flow of the gas was controlled by connecting the cylinder to the gas burner through a capillary tube. No stop-cock was connected in the SO_2 line, the capillary being selected by trial to give the desired rate of flow.[1] The percentage of SO_2 in the furnace atmosphere was fixed from analyses made during the early part of each run before the furnace had reached a temperature at which partial conversion to SO_3 took place.

Mounting of Cones Great pains was taken to see that the cones were mounted exactly in a prescribed manner. The plaques for use below 1450°C were made of equal parts of kaolin and Carborundum with a small addition of ball clay, and for higher temperatures they were made of ground Alundum and Norton 518 cement. Precaution was taken to make up the pat material with as little water as possible.

After marking each large cone at two inches from the tip it was pushed into the pat to this mark, and the numbered face of the cone was placed against a template so that it made an angle of 82° with the surface of the pat. (See Fig. 3.) Some of the pat material was then used to fill the holes around the base of the cone and the surface of the pat was carefully smoothed. After setting up the cones the pat was dried at 105°C over night. Following this they were placed in one of the furnaces and carefully adjusted so that the marked faces were 8° from vertical, by sighting past the template resting outside the furnace upon a levelled platform.

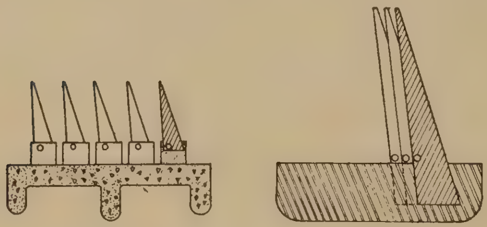

FIG. 3.—Cross-sections of mounted cones.

The small size of cones 23 to 42 made it necessary to mount them in the special manner shown also in Fig. 3, in order that the small holes bored in their bases would not interfere with the bending. They were mounted with their tips $\frac{3}{4}$ inch above the upper surface of the small bases and the top edges of the holes $\frac{1}{32}$ inch below the surface. The end point of a small cone thus mounted was taken as the temperature at which the tip of the bending cone passed the level of the upper surface of the small base. A few of the most refractory of these small cones do not bend over in fusing but show the first signs of fusion by a rounding of the tip, which is followed by a melting down of the cone into a compact rounded mass. The end point in such a case may properly be taken as the temperature at which the last trace of the original shape disappears into a rounded mass. At this temperature the change in shape is proceeding at a visible rate.

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[1] The furnace gases were analyzed for SO_2 by absorption in an iodine solution containing iodine per cc equivalent to .0675 cc of SO_2 gas. The percentage of SO_2 was calculated from the volume of furnace gases required to just decolorize 20 cc of this solution in an absorption tube.

The rates of heating were controlled with particular care during the time the cones were bending, and, depending upon the characteristics of each cone, for a considerable period before bending commenced. In order to avoid the small fluctuations in temperature caused by automatic control, hand control, as stated above, was invariably used for the last few hours of each run, the constant attention of the observer then being required. The 20° rate of heating was maintained during this period to the nearest degree and the faster rate of 150° per hour to 5°, without any sudden irregularities.

Summary of Observations and Tabulated Data

Much of the information obtained has been put in tables of temperatures and cone numbers.

Tables I and II giving the individual observations on the end points of cones 022 to 1, heated in air, are included to show the order in which the work was carried out and the precision which was attained in the temperature measurements. In all the remaining tables of numerical data the individual readings have been averaged in groups and the means have been rounded to the nearest five degrees. The differences in end points obtained under different heating conditions were taken from the unrounded means and are given in the tables without rounding because in many instances the results appeared to be good to a few degrees and rounding tended to obscure some of the relations which it was desirable to point out.

Observations of the colors of the fused cones and the manner of bending, bloating, etc., are summarized in Tables III, V, VIII, and IX.

The gaseous atmospheres employed are indicated in the tables, simply as per cent of CO_2 in the dry gas. The composition of the Washington gas is sufficiently constant for this purpose. From the analysis of this gas the compositions of the products of combustion with excess of air giving 10%, 5%, and 3% CO_2, dry, are found to be approximately:

9%CO_2, 12%H_2O, 7%O_2, 72%N_2, (10% CO_2)
4.5% CO_2, 7% H_2O, 13.5% O_2, 75% N_2, (5% CO_2)
3% CO_2, 5% H_2O, 16% O_2, 76% N_2, (3% CO_2)

Discussion of Results

Cones 022 to 011 Heated in Air

See Tables III and IV. These cones will bend in a normal fashion if they are fired slowly enough in an atmosphere containing sufficient oxygen to allow oxidation of the organic binder before vitrification and the development of a vesicular structure take place. Heating in air at 20° per hour will give good results but it is not necessary to maintain so slow a rate before oxidation or vitrification begins nor after oxidation is complete. The exact limits which assure complete oxidation and the absence of bloating were not determined. Only cones 022 and 021, which begin to vitrify at very low temperatures, require particularly careful firing.

A small amount of bloating of these cones will not affect the end points. They will, in fact, come down at the correct temperatures even if at temperatures a few degrees above the end points, they are bloated to two or three times their original size. In such cases, however, they do not bend normally, because of slight bloating below the end point, and if mounted improperly they will bloat at the base even during the initial bending.

Differences Due to Rate of Heating

Cone 022 contains no clay but is made entirely of a soft glass which is also used for cones 021 to 016 in decreasing percentages. With this series the differences in end points observed at the two rates of heating vary with fair regularity from 18° for cone 022 to 58° for cone 016. That is, the differences increase as the content of glass, or flux, decreases, which is just the reverse of general statements which are found in the literature touching upon this point. The observed regularity is probably due to the fact that there is no volatilization of B_2O_3 nor any reaction between the glass and kaolin at the low temperatures at which these cones fuse.

This relation does not hold for cones 015 to 011 which fuse at higher temperatures and which, moreover, are made of a different glass. In these five cones the relation is apparently upset by some reaction which, in the case of cone 012, proceeds fairly rapidly while the cone is bending, so that, with slow heating the bending interval is 85° and the end point is higher than that observed during rapid heating. Unfortunately, the end point, for slow firing is also higher than that of the next cone, 011.[1] Again, in cone 011, the reaction proceeds so rapidly that with rapid heating the end point is normally higher than with slow heating, and is even higher than that of cone 010 for rapid heating. The data indicate that under very slow firing cone 020 may also get out of its proper order, and it appears that the fusibility of cones 019 and 018 should be decreased, particularly that of 019.

In general, for this series the temperature intervals of bending are nearly the same for both rates of heating. That is, during bending, the change of consistency or deformability with temperature roughly follows a general law. Of course, this law is not obeyed when reactions occur as in cone 012. It will be noticed that the temperature intervals of bending and the differences of end points for the two rates selected vary in such a way that the starts of bending observed at one rate do not indicate end points for some slower rate. In a few cases the end points observed during slow heating are considerably lower than the "starts" observed during rapid heating, a fact which supports the statement that the "starts" are not precisely determinable.

If a series of cones such as 022 to 017 were all made of an inert material and a stable fusible glass, all the cones could be "brought down" by long-continued heating at a temperature where the glass is appreciably fluid. Such a tendency is indicated in this series as it is now made. At higher temperatures where glass and clay react, such a tendency is, in general, lessened by the reaction.

For such reasons as these, the "load test" for refractory materials has been developed, and in the next section the results of such a test of cones 08, 09, and 010 are given.

Cones 010 to 01 Heated in Air

See Tables IV and V. Each cone of this series is a complex mixture of glass, feldspar, iron oxide, whiting, kaolin, and flint; that is, SiO_2, Al_2O_3, CaO, Fe_2O_3, K_2O, Na_2O, and B_2O_3 with small amounts of impurities.

The "bending intervals" and the "cone intervals" of this series are fairly uniform, but the differences between end points for slow and fast heating can be grouped; cones 010, 09, and 08 are not much affected by the range of heating rates tried, cones 07, 06, 05, and 04 show differences of 10°, and the last three, 03, 02, and 01, differences of 30 to 35°. Thus the differences for the groups are 1–5°, 10°, and

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[1] The manufacturer furnished a second lot of cones 012, which do not show these abnormal characteristics. The end point of this cone as it is now being furnished by the manufacturer is 840°C for the 20° rate of heating, and 875°C for the 150° rate. The start of bending is 790° for each rate. Thus the right order of refractoriness is restored, and the reaction previously indicated now manifests itself only in the long bending interval (85°) under rapid heating.

30–35°, a gradation roughly similar to that noted for the most fusible cones. The sudden change from cone 04 to 03 is accounted for by the greater difference in composition between these two cones than between any other successive cones of the series.

These cones contain in smaller proportions the same glass that is present as a large fraction of cone 015 which begins to bend at about 740°C, more than 100° below the start of cone 010. This relatively fusible glass evidently reacts with other constituents at a temperature far below the fusion range of the members of this series, so that the compounds formed are less fusible than one of the constituents originally present. Sosman has mentioned that such reactions are desirable in compounding cones which will not fuse sharply.

A load test applied to these cones should distort them at 740°C. It was tried on cones 08, 09, and 010, which were mounted horizontally in the furnace and loaded near their tips, each with a 25 gm. weight. All three started to bend at 741°, a perfect demonstration of the utility of the load test for fusible constituents of refractory materials.

The cones of this series all fused in a normal fashion in air, and hence no difficulty was met in checking the determinations of the end points to a few degrees.

Cones 1 to 42

See Tables VI and XII. In this group, cones 1, 2, and 3 constitute a single series, 5 to 28 another, 29 and 30 contain only clay, flint, and feldspar, 31 to 34 contain clay and flint, and 36 to 42 contain clay and alumina. Cone 4 is unique. Cone 35 is pure kaolin.

Within experimental accuracy, all cones above No. 1 fused at the same temperature in a gas containing 10% CO_2 as in air, hence the rsults have been averaged and the means arranged in a single table (VI).

The cone intervals are somewhat more uniform than those of the lower series.

The bending intervals of the first three members (1, 2, and 3) of this series are constant from cone to cone for each of the two rates of heating. The differences in end points for fast and slow heating decrease from 35° for cone 1 to 25° for cone 3. This and the fact that there are no reports of these three cones showing a tendency to come down together seem to indicate that the principal fusing ingredient in them is formed during their fusion.

On the other hand the differences in end points (fast minus slow) of cones 4, 5, 6, and 7 increase decidedly from one cone to the next, and Seger, Orton, and Rieke have stated that these few cones show a tendency to come down together.

Discussion of Differences in Fusing Behavior

Cone 9, when heated at 150° per hour, is bending for about 45 minutes and the difference in end points for the two rates has dropped again, which indicates the formation in this cone of a new compound or eutectic mixture melting at about 1250°C.

Cones 10, 11, and 12 show an initial warping which seems to precede ordinary bending, a behavior which may be related to the reaction presumed to take place in cone 9. Sosman has surmised the presence of a eutectic containing lime, alumina, and silica in cones 11 and 12.

Cone 13 stops bending for a few minutes when about half way down, and seems to melt rather sharply after this pause, at 1350°C, at least there is a negligible difference in the end points for the two rates of heating. This indicates a new reaction in cone 13.

In cones 15, 16, and 17, it appears that still another reaction is beginning but that it proceeds very slowly until a temperature of about 1485–1490° is reached, because cone 17 bends so slowly that the start can only be guessed and cone 18 has the same end point for the two rates of heating.

The precision attained in determining the end points above 1500°C is not great enough to give real significance to the differences in these points for cones 19 and 20.

The somewhat speculative statements in the preceding paragraphs are not idly made; they call attention to the plain facts that each cone is a little different from its neighbor and that any general statement describing the manner in which cones fuse should be limited to a small number in a short series.

Cones 23 to 38 were heated at 100° per hour, no attempt being made to study the effect of slow heating of these refractory cones whose bending intervals are generally much shorter than those of the lower series.

Sosman showed in a very simple manner that cones 28, 29, 30, and 31 could all be brought down at 1615°C, which is now found to be the end point of cone 28 heated at 100° per hour. From the experiments of Bowen and Greig[1] who discovered a eutectic of cristobalite and mullite melting at 1545°C it appears that cones 23, 26, and 27 and perhaps even higher ones could be brought down at 1545° or lower. The present authors have often observed in their laboratories that refractory pyrometer-tubes formerly called sillimanite porcelain, all bend at 1540° or lower.

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[1] *Jour. Amer. Ceram. Soc.*, **7**, 238 (1924).

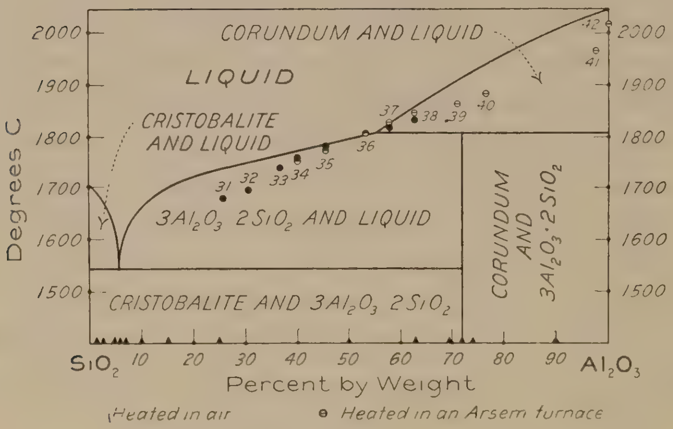

FIG. 4.—Equilibrium diagram of system $Al_2O_3 - SiO_2$, by Bowen and Greig, with end points of cones 31 to 42 plotted.

Bowen and Greig have explained these observations. Cones 31 to 42, which consist of the simple binary system Al_2O_3–SiO_2, can be placed as shown in Fig. 4 on the Bowen and Greig equilibrium diagram. It is evident that the lower cones of the series contain enough liquid above 1545° to come down at temperatures well below the liquidus when heated at 100° per hour, while cones 35 to 37 fuse so sharply that their end points lie very near the liquidus curve, and in fact agree with the curve within experimental error. Some of the cones above 36 would in all probability come down after a period of heating at 1810° or a few degrees higher, if they were not contaminated or in some way altered by heating at so high a temperature.

Cones 39 to 42 were not tested in an oxidizing atmosphere, but only in an Arsem furnace in which the atmosphere is highly attenuated although still somewhat reducing. Because of a slight reducing action of this atmosphere it is necessary, in order to minimize carbonization, to heat the cone material in the form of compact cylinders at a very rapid rate; hence, it is reasonable to expect that the deformation points determined thus will differ somewhat from the end points determined in air at a slower rate of heating. Therefore, to compare the two methods of heating, cones 34 to 38 inclusive were tested in the Arsem furnace after determining their end points in air. The results were very satisfactory and the subsequent measurements on cones 39 to 42 can properly be regarded as fairly trustworthy.

Cones 022 to 01
Heated in Furnace Gases

See Tables VII, VIII, IX, and X. Cones 022 to 017 exposed to the action of furnace gases containing 10% CO_2 behaved rather regularly when heated slowly but the first four of these were not fused successfully in such an atmosphere at 150° per hour. Cone 016 and possibly also 017 and 018 fused abnormally low in this atmosphere.

Cones 015 to 011 fused at too high a temperature when heated slowly, but when heated rapidly they bent and fused in a normal manner. Cone 012 was an exception to this, that is, when it was heated rapidly it fused more than 20° lower than when it was heated slowly, while the difference was only 8° when the cone was heated in air.[1] These differences between end points for fast and slow heating show the same general trend as those given in Table IV.

The data in Table VII show, as one might expect, that the effect of furnace gases depends upon their concentration and the time of exposure of the cones. Therefore, since the effects on cones 022 to 011 of an atmosphere of 10% CO_2 were generally small, and also since the differences in end points ("gas minus air") were in some cases within experimental error, none of this group was tested in an atmosphere of 5% CO_2.

Cones 010 to 01 were all stiffened on the surface by slow heating in 5% CO_2 and two of this group, 010 and 09, acted so erratically that the results were thrown out and in their place those obtained from special runs with only 3% CO_2 were substituted.

With slow heating the results on cones 08 to 01 show, when the experimental error is considered, what may be a gradual decrease in the effect of 5% CO_2, cone 01 being affected scarcely at all. The actual figures show, however, a maximum effect at cone 06, which is coincident with a maximum in the lime content.

With rapid heating in this atmosphere there is a gradual increase in the effect of CO_2 from cone 010 to 04, which is consistent with the gradual increase in the proportion of the more basic constituents present in each cone. At cone 03 there is a marked change in composition, to a higher percentage of clay, and possibly as a result of this change, cones 03, 02, and 01, as the data show, were not perceptibly altered by CO_2. Because the percentage of each constituent varies from one cone to the next, it is almost impossible to ascribe the effect of furnace gases to any single one of them.

The results obtained upon heating cones 09 to 04 in 10% CO_2 at 150° per hour are so unsatisfactory as to be almost worthless, showing that these cones should not be used under such conditions. Each value given in the table for this set of conditions is the mean of many repetitions; individual results varied in a few instances by 10° from the mean, and many results were cast out because of the manner in which the cone "came down." Most of the cones were so severely attacked by the furnace gas that they bent scarcely at all, except at the base where the skin broke or burst. That part of the cone protected by the pat fused first and, in bloating, burst the hardened surface.

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[1] See foot note 1on page 715.

The descriptions of bending, bloating, and surface action, given in Tables VIII and IX, are brief but probably sufficient. It is impossible to be very exact in these descriptions.

Effect of SO_2

See Table X. M. C. Booze, Research Fellow at Mellon Institute for the Refractories Manufacturers Association, kindly sent out numerous inquiries concerning the amount of SO_2 in kiln gases. The information available was meager, but it supplied a reasonable basis for the selection of a proportion of SO_2 which would be roughly representative of conditions commonly met. Much of the sulphur found in the gases of some kilns comes from the ware; in such cases the composition of gases which surround cones in the kilns is a matter of doubt. However, it was thought that experiments with furnace gases containing 0.3 or 0.4% of SO_2 would supply the information sought.

Only a selected number of cones (see Table X) were subjected to sulphur-bearing gases. All these, with the exception of cone 011 which has a very small content of bases, fused at *higher* temperatures in such gases than in gases containing no appreciable percentages of sulphur. The differences given in the third and in the last columns of Table X represent the contributive effect of SO_2, that is, the differences in end points found in gases free from sulphur from those found in gases carrying sulphur.

Cones 017 and 016 were apparently unaffected by SO_3 or SO_2 so that the end points agreed with those observed when these two cones were heated in 10% CO_2 free from the sulphur oxides. The surface of cone 015 was attacked slightly and its end point was raised about 8°.

Cones 011, 010, and 09 were attacked severely and came down stiff. The end points observed under such a condition are of little value and the differences given in the table for these three cones should be regarded as merely indicative of the magnitude of the effects. The first two of these had a very thick, hardened skin with a "normal color" but where the skin burst at the base the inside appeared green or greenish yellow. In some cases the inside fused and ran out at the base of the cone.

Cones 02 to 4 bent and arched fairly well, the last three of the group bending the most nearly in a normal manner. The surfaces of all but the last, No. 4, were glassy and bumpy, and all were green, even cone 4 which contains iron only as an impurity and is white when fired in sulphur free gases. The green color varied from the fairly deep shade produced in 02 to the very light shade in No. 4.

Cones 18, 19, and 20 bent mostly at the base and were perceptibly stiffened so that their end points were raised by 25°, indicating that there must have been a considerable absorption of SO_3 even at these high temperatures. No analyses of the fused cones were made, but there is no doubt that sulphates were formed. Orton[1] states that in one instance 2.5% of SO_3 was found in a cone which had been exposed to furnace gases containing sulphur oxides.

It seems strange that the surfaces of cones whose end points are raised by the action of SO_3 should be glassy when the cones are heated in an atmosphere containing this oxide. Only a detailed study of the action of the acid-forming oxide could furnish a satisfactory explanation of this enigma. The authors suggest, with diffidence, that SO_3 was dissolved in the original glass constituent of the cones, that this effect increased the solubility of certain particles otherwise relatively insoluble, and by so doing produced a glass having an increased viscosity.

Note on Grinding Off the Surface of a Cone before Using

Three No. 7 cones were mounted on a pat, one cone unaltered, one whose three sides had been sand-papered to remove the original surface, and one from which the surface of one side only had been removed. These were heated at 20° per hour in an atmosphere of 3% CO_2 (no SO_2) with the result that all were observed to come down together, that is, within experimental error, to "fuse" at the same temperature. This experiment was made to answer a question regarding the action of the original surface, raised during the course of the work. It seemed unnecessary to study this question further.

General Discussion

In firing clay ware the fundamental thing is the following of a prearranged time-temperature schedule and the final attainment of a certain temperature. Time is easily measured with the required accuracy, hence the process is fundamentally one of temperature control.

Pyrometers Temperatures are generally estimated by observing or measuring a physical change in a pyrometric device whose physical condition can be kept independent of all other factors but temperature. There are only a few principal types of temperature measuring instruments: (1) gas, liquid, and vapor thermometers, (2) resistance thermometers, (3) thermoelectric pyrometers, (4) radiation and optical pyrometers. These various types or kinds can be placed in two classes, namely, (1) the device itself is raised to the temperature being measured, and (2) the device is not raised to the temperature measured, but is used to gage the intensity of radiant energy, heat, or light, emitted by the hot body or furnace. Devices of the first class are inherently unsuitable for the measurement of temperatures above certain limits; the higher the temperature, the more difficult it is to find a substance which can withstand the high temperature without permanent change, or without change which is dependent on other things than temperature. For example, when a thermocouple is used at high temperatures it is always subjected to some alteration or contamination.

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[1] *Trans. Amer. Ceram. Soc.*, **3**, 198 (1901).

Thermocouples Do Not Give Same Readings Under All Conditions

One does not hesitate because of this to standardize or calibrate thermocouples, even though under some conditions, their performance may not be wholly satisfactory. Such calibration is carried out under definite and reproducible conditions, so selected that the performance of the thermocouple during the tests will be as satisfactory as possible. However, thermocouples are checked under actual conditions of use, whatever they may be, to determine as accurately as possible the corrections to the original calibration, which should be applied at the time of the check.

Standardizing Cones Same in Principle as for Thermocouples

Hence, one does not hesitate to determine the behavior of pyrometric cones under definite and reproducible conditions, and to determine also the magnitude of those errors which may be met during their use. In the present investigation, the cones, each one always mounted in a definite manner, have been heated at carefully controlled rates in clean air. This simple set of conditions can be maintained and reproduced with relative ease.

Rieke said that the end points of cones could never be determined once for all. The two principal reasons for this statement are: (1) cones are artificial mixtures not always the same but only approximately so, and (2) their defined end points are not invariants but depend upon rate of heating and, to some extent, upon furnace atmosphere, which may contaminate their substance.

It is believed that the confusion which has persisted in regard to the characteristics and proper function of cones is caused not only by the lack of accurate numerical data obtained under known conditions, but also by the complexity and variety of their reactions and the large number of different cones in common use, each having its own peculiarities. The confusion is undoubtedly augmented by the refusal of many ceramists to think in terms of temperature, and also by the practice in their industry of using an indefinite scale of refractoriness while all other heat-process industries use a scale of temperature. Seger warned against this practice nearly forty years ago when discussing use of Bishof's standard refractory clays.

The following quotation from Day and Sosman[1] regarding the behavior of slow-melting substances, is repeated:

> The so-called melting interval of slow-melting compounds (quartz, albite, orthoclase) should be carefully distinguished from the "melting interval" of mixtures (lime-soda feldspars, impure natural minerals). The former melt and become amorphous very slowly, but their melting interval is an interval of *time*, whereas the melting interval of mixtures is an interval of *temperature*. The pure soda feldspar (albite) if held at a temperature slightly above its melting point for a sufficient length of time, will melt completely; the mixture, on the other hand, if held at a temperature within its melting interval, will melt in part, come to equilibrium, and remain indefinitely part crystalline and part liquid.

Pyrometric cones are, with few exceptions, mixtures; hence, the melting range or interval would be described as one of temperature. However, this is a secondary consideration because a cone always comes down before it is completely melted. It may come down after exposure for an interval of time at a constant temperature and in such cases its behavior resembles somewhat that of a slow-melting compound, but the cone in practical use is generally subjected to heating at a slowly rising temperature. Now, whether the temperature is rising or is constant the cone bends over slowly; consequently the end point is variable depending upon time, temperature, and atmosphere.

Rieke stated that cones are more or less like the ware. The cones differ from the ware, however, in that the cones must "fuse" while the ware is "maturing." If the ware at a certain schedule of heating is properly matured at the end point of some particular cone this schedule should be maintained. Experience has shown that if another schedule is followed the ware may not be properly matured at the same cone.

Cones Measure Temperatures and Not Effect on Wares

If the same schedule is followed and the kiln gases are the same the cone will always come down at the same temperature. Thus it measures the temperature at which the ware will mature with a controlled rate of heating and given character of kiln gases. It does not measure the combined effect on the ware of time, temperature, and kiln gases. Since its performance depends upon these three factors, the cone may, to some extent, serve to gage roughly their effects on the ware.

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[1] *Amer. Jour. Sci.*, **31**, 341 (1911).

It may even be thought by some that in many cases the cone and the ware are so nearly similar that, for practical purposes, they may be regarded as identical, but experience proves that this is not the case and that the cone cannot be properly regarded as a true gage of the progress of the maturing of the ware. As examples of differences which can be expected between the cone and the ware, the differences in the characteristics of cones themselves may be cited, such as numbers 04 and 03, 8 and 9, 12 and 13, and lastly 010 and 011 fired in an atmosphere containing 0.35% of SO_2. (See Table X.)

The cones constitute a complete series of standard mixtures each of which will always, within tolerable limits, respond consistently to different conditions of firing, but they will not in respect to different conditions of firing in the same manner and degree as will the ware.

Effect of Contamination by Furnace Gases The contamination of cones by furnace gases free from sulphur is ordinarily not serious because there is generally a fairly large excess of air in a ceramic kiln. The behavior of the higher cones indicates that they are little affected by a "neutral" or even slightly reducing atmosphere.

The effects of gases containing SO_2, shown in Table X, are both surprising and disappointing. The SO_3, which is probably the more active of the two oxides, proves to have a very powerful influence on the viscosity of the silicate mixtures. Certainly the effects of SO_2 (SO_3) in kiln gases should be studied more extensively than in the present investigation. They should be studied with simple and pure compounds, to prove, for instance, whether or not lime is especially to be blamed for the difficulty with SO_2, as has been guessed by others, and whether B_2O_3 is replaced and driven off by SO_3, and whether an iron oxide or silicate acts as an efficaceous catalyzer.

The data in Table X indicate that the end points of cones in kiln gases can be relied upon, in most cases, to about 25° if the SO_2 content is not greater than 0.3%. Fortunately there is a warning in the result obtained on cone 011 not to draw the general conclusion that SO_2 always raises the end point.

Comparison of Old Data with Present Results

An interesting comparison of all the principal data is presented in Table XI. In the old data more than one make of cones is represented and in no case were the conditions of heating clearly specified or controlled with sufficient accuracy; nevertheless, the differences between those data and the present results are, on the whole, remarkably small, a fact which requires explanation.

The differences in the data shown in column 2 of Table XI are small up to cone 26, because in the time of Seger a few of these cones were compared with well-established melting points of metals. Above 1500°, the temperature scale was very uncertain, and for this reason the values given in the original circular for the highest cones were almost pure guesses and differed from the values obtained by us by as much as 80°C.

In 1910, the values as amended were supposed to fit slow firing in industrial kilns, and from cones 1 to 35 the agreement with the present results for slow firing in furnace gases is excellent.

The almost consistently high values of Hofmann (1907–1909) were obtained with a rate of heating of 300° an hour, and hence they *should be* generally higher. Hofmann's 1911 tests in industrial kilns were made without control of the rate of heating which was probably slower than 20° per hour.

Rieke, in 1911, used fuel-fired kilns without any adequate control; hence, the present authors feel justified in averaging all of Rieke's data for slow rates. His individual results varied far outside the differences shown in Table XI.

Brown and Murray, in 1913, either allowed their kilns to heat more slowly than they intended near the end-points of the cones or else their temperature measurements are in error, for it is unlikely that such large differences as appear in column 7 could be caused by differences in furnace atmospheres alone; moreover, the uniformity of the differences in this column point to errors in temperature measurements because the cones would not respond with such regularity to differences in heating conditions.

Fieldner, Hall, and Feild heated the cones at a very rapid rate and thus obtained high results, but even so their result for cone 8 is evidently too high.

Cone 35 and Kaolin

Cone 35, which has a fairly sharp melting point, has always been made from pure grades of kaolin, hence comparison of the various determinations of the end point of this particular cone is significant. The data are given in Table XII.

The melting points given for the various samples are quite consistent with the analyses. The analysis given by Seger for Zettlitz kaolin, which analysis probably fits the material tested by Hofmann, is:

	Per cent		Per cent
Silica	46.87	Magnesia	trace
Alumina	38.56	Alkali	1.06
Iron oxide	0.83	Loss on ignition	12.73
Lime	trace		

The analysis by the Bureau of Standards of the Florida kaolin used for Orton cone 35 is:

	Per cent		Per cent
Silica	46.83	Magnesia	trace
Alumina	40.83	Total alkali	0.24
Iron oxide	0.65	Loss at 105°	0.60
Titanium oxide	0.34	Loss on ignition	10.56
Lime	0.20	Phosphoric anhydride not detected on one gram	

The figure 1770° given in the 1910 circular of the *Tonindustrie Zeitung* is probably the value accepted at that time for the melting point of platinum, for it was known then that cone 35 melted very nearly at the melting of that metal.

Summary

The characteristics of pyrometric cones have been determined under definite and reproducible conditions of heating. The temperatures of the "end points" of a complete set of cones together with their bending intervals were measured at carefully controlled rates of heating in clean air and in various kiln gases.

With a few exceptions the end points were found to be higher when the rate of heating was 150°C per hour than when the rate was 20° per hour. The maximum difference in this investigation is only 58°, and in but five cases is the difference more than 40°. In many instances the differences are almost negligible or within experimental error.

Under slow heating in gases free from SO_2 the end points of cones 015 to 01 are somewhat higher than those found in clean air. Cones 022 to 016 and 1 to 42 were acted upon only slightly by kiln gases free from SO_2.

A standardized method of testing has been developed, which is applicable not only to the examination of cones but to testing for the refractoriness of any ceramic material or product. The accuracy obtained by this method was better than 5° up to 1400°C and better than 10° from that temperature up to 2000°.

Each cone should be considered separately. "Cone intervals" and "bending intervals" should not be taken as uniform for all the cones but as shown for each in the tables here given.

Cones are properly used only for the measurement of temperatures. The cones will always come down at the same temperatures if the same heating schedule is always followed and if there have been no effects from the variations in the kiln gases.

A cone in a kiln does not measure the combined effect of time, temperature, and kiln gases upon the progress of maturing of the ware.

The combined use of cones and pyrometers is recommended for kiln control, but the authors believe that cones are inherently unsuited to laboratory tests of the refractoriness of clay products.

TABLE I

END POINTS OF CONES IN DEGREES CENTIGRADE
(Rate: 20°C per hour)

Cone No.	Sept. 10–11	Sept. 12–13	Sept. 15–16	Sept. 19–20	Sept. 22–23	Sept. 24–25	Sept. 26–27	Sept. 29–30	Oct. 1–2	Oct. 6–7	Oct. 8–9	Mean	Max. diff. from mean
022	586	588	——									587	1
021	595	595	591									594	3
020	622	628	625	620								624	4
019				626	628							627	1
018				669	671							670	1
017					716	721						718	3
016						737	735					736	1
015						773	770					772	2
01							796	795				795	1
013								825	824			8 5	1
012*		Aug.	Aug.	Aug.	Aug.			884	888	——	883	8 5	3
011		11–12	13–14	15–16	18–19	Aug.	Aug.	Aug.	876	875	871	874	3
010		890				20–21	22–23	25–26		891	886	889	3
09		927						928				927	1
08		946						944				945	1
07			978					977				977	1
06			1001				1006					1004	3
05			1029				1032					1030	2
04				1051			1054					1052	2
03				1082	1082							1082	0
02				1097	1093	1098						1096	3
01					1115	1108						1111	4
1						1126						1126	–

*See foot note page 715.

TABLE II

END POINTS OF CONES IN DEGREES CENTIGRADE
(Rate: 150°C per hour)

Cone No.	Oct. 10–11	Oct. 13–14	Oct. 15–16	Oct. 17–18	Oct. 20–21	Oct. 22	Oct. 24	Oct. 28	Oct. 29	Oct. 30	Mean	Max. diff. from mean
022	603	603	608								605	3
021	620	615	617								617	3
020	647	650	652	647							649	3
019				661	663						662	1
018				718	719						718	1
017					770		775				772	3
016						794	793				794	1
015						807	807				807	0
014						829		828			828	1
013								860	861		860	1
012*	June	June	June					876	876	878	877	1
011	18	19	20	June					905	905	905	0
010	895	894		21						899	896	3

*See foot note page 715.

Cone No.	June 18	June 19	June 20	June 21	June 23	June 24	June 25	June 26	June 27	June 28	Mean	Max. diff. from mean
09	928	925	934								929	5
08	953	946	950	956							951	5
07			987	989	987						988	1
06				1011	1015	1019					1015	4
05					1040	1040	1037				1039	2
04						1063	1062	1062			1062	1
03							1114	1116	1114		1115	1
02								1128	1124	1126	1126	2
01									1144	1147	1146	2
										1147		

TABLE III

BEHAVIOR OF CONES 022 TO 011 HEATED IN AIR

Cone No.	Heating rate, °C/hr. up to temp. in next column	Rate changed at this temp. to that in next col.	Rate maintained to end point	Bending: Arching	Bending: At base	Bloating: Before end point	Bloating: Above end point	Remarks
022	70°C	230°C	20°C	Fair	Slight	slight	40°C severe	OK
	125	500^1	20	Bad	N	—	—	6°C low
	40^2	500^2	150	Fair	Slight	slight	—	OK
	42	510^3	150	"	"	"	—	OK
	500	500^4	150	bad	?	"	—	OK
021	70	230	20	N	N	none	30°C slight	OK
	125	500	20	N	N	"	—	OK
	40^2	500^2	150	N	N	"	none	OK
	42	510^3	150	N	N	"	"	OK
	500	500^4	150	bad	?	slight	severe	8°C low
	125	525^5	150	"	?	"	"	7°C low
020	70	230	20	N	N	none	—	OK
	125	500^1	20	N	N	"	—	OK
	200	230	20	N	N	"	50°C none	OK
	40^2	500^2	150	N	N	"	—	OK
	42	510^3	150	N	N	"	—	OK
	500	500^4	150	—	—	severe	—	2°C low
	125	525^5	150	—	—	"	—	7°C slight
	20	500^6	150	N	N	none	70°C slight	OK
019	200	230	20	N	N	"	—	OK
	70	215	20	N	N	"	—	OK
	20^6	500^6	150	N	N	"	60°C slight	OK
018	200	230	20	N	N	"	—	OK
	70	215	20	N	N	"	—	OK
	20^6	500^6	150	N	N	"	50°C none	OK
017	70	215	20	N	N	"	—	OK
	160	160	20	N	N	"	—	OK
	20^6	500^6	150	N	N	"	—	OK
016	160	160	20	N	N	none	none	OK
	110	440	20	N	N	"	"	OK
	250	500^7	150	N	N	"	"	OK
	20^8	680	150	N	N	"	"	OK

TABLE III (*concluded*)

Cone No.	Heating rate, °C/hr. up to temp. in next column	Rate changed at this temp. to that in next col.	Rate maintained to end point	Bending		Bloating		Remarks
				Arching	At base	Before end point	Above end point	
015	160	160	20	N	N	none	none	OK
	110	440	20	N	N	“	“	OK
	250	500[7]	150	N	N	“	“	OK
	20[8]	680	150	N	N	“	“	OK
014	110	440	20	N	N	“	“	OK
	100	300	20	N	N	“	“	OK
	250	500[7]	150	N	N	“	“	OK
013	100	300	20	N	N	none	none	OK
	250	390	20	N	N	“	“	OK
	250	500[7]	150	N	N	“	“	OK
	250	560	150	N	N	“	“	OK
012	100	300	20	N	N	none	none	OK
	250	300	20	N	N	“	“	OK
	250	500[7]	150	N	N	“	“	OK
	250	560	150	N	N	“	“	OK
011	250	300	20	N	N	none	none	OK
	90	300	20	N	N	“	“	OK
	250	560	150	N	N	“	“	OK

N = Normal
OK = Data used

[1] Held 14 hours at 500°C

[2] 60°C/hr. to 465°C (held 18 hours) and at 500°C held 4 hours

[3] Held 14 hours at 510°C

[4] Held $2\frac{1}{2}$ hours at 500°C

[5] Held 3 hours at 525°C

[6] 130°C/hr. to 265°C, held 1 hour at 500°C

[7] Held $1\frac{1}{2}$ hours at 500°C

[8] 80°C/hr. to 350°C

TABLE IV

END POINTS AND INTERVALS OF CONES 022 TO 01 (Heated in Air)

Rate °C/hr. Cone No.	20°C End point	150°C End point	Diff. fast–slow	20°C Bending interval	150°C Bending interval	20°C Cone interval	150°C Cone interval
022	585°C	605°C	18°C*	45°C	55°C	10°C	10°C
021	595	615	23	45	45	30	35
020	625	650	25	30	25	5	10
019	630	660	35	30	20	40	60
018	670	720	48	30	30	50	50
017	720	770	54	30	30	15	25
016	735	795	58	35	55	35	10
015	770	805	35	30	45	25	25
014	795	830	32	45	40	30	30

TABLE IV (*concluded*)

Rate °C/hr. Cone No.	20°C End point	150°C End point	Diff. fast–slow	20°C Bending interval	150°C Bending interval	20°C Cone interval	150°C Cone interval
013	825	860	36	45	50	60	15
012§	885	875	− 8	85	45	−10	30
011	875	905	31	65	65	15	−10
010	890	895	7	30	25	40	35
09	930	930	1	35	40	15	20
08	945	950	6	55	60	30	40
07	975	990	10	35	50	30	25
06	1005	1015	11	25	35	25	25
05	1030	1040	9	30	30	20	20
04	1050	1060	10	40	40	30	55
03	1080	1115	33	40	35	15	10
02	1095	1125	30	35	35	15	20
01	1110	1145	36	50	45	15	15

*Values not rounded as in columns 2 and 3.

§See foot note page 715 regarding a second lot of cones 012.

TABLE V

HEATING SCHEDULE AND BEHAVIOR OF CONES 010 TO 4 HEATED IN AIR

Cone No.	Heating rate, °C/hr. up to temp. in next column	Rate changed at this temp. to that in next col.	Rate maintained to end point	Behavior	Color	Remarks
010	41°C	725°C	20°C	N	Chestnut brown to olive—20° per hour Brown to russet—150° per hour	OK
	90	475	20	N		OK
	250	560	150	N		OK
	270[1]	670	150	N		OK
09	41	725	20	N		OK
	35	825	20	N		OK
	270[1]	670	150	N		OK
08	41	725	20	N		OK
	35	825	20	N		OK
	270[1]	670	150	N		OK
07	43	280	20	N		OK
	35	825	20	N		OK
	270[1]	670	150	N		OK
06	43	280	20	N		OK
	40	905	20	N		OK
	270[1]	670	150	N		OK
05	43	480	20	N		OK
	40	905	20	N		OK
	270[1]	670	150	N		OK
04	39	955	20	N		OK
	40	905	20	N		OK
	270[1]	700	150	N		OK
03	39	955	20	N		OK
	40	990	20	N		OK
	330[2]	1045	20	N	Special test	OK
	270[1]	800	150	N	olive	OK
02	39	955	20	N	“	OK

TABLE V (*concluded*)

Cone No.	Heating rate, °C/hr. up to temp. in next column	Rate changed at this temp. to that in next col.	Rate maintained to end point	Behavior	Color	Remarks
	40	990	20	N	olive	OK
	40	1015	20	N	“	OK
	330[2]	1045	20	N	Special test	OK
	270[1]	800	150	N	olive	OK
01	40	990	20	N	“	OK
	40	1015	20	N	“	OK
	330[2]	1045	20	N	Special test “	OK
	270[1]	800	150	N	buff-olive	OK
	450	900	150	N	brown-green	OK
1	40	1015	20	N	buff-olive	OK
	430	1010	20	N	“	OK
	450	900	150	N	brown-green	OK
2	430	1010	20	N	–	OK
	450	900	150	N	yellow-green brown tinge	OK
3	430	1010	20	N	buff-olive	OK
	450	900	150	N	light yellow-gray	OK
4	430	1010	20	N	white	OK
	450	900	150	N	“	OK

OK = data used

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[1] Heated to 400°C in 1 hour

[2] Heated to 675°C at 500°C per hour

TABLE VI
CONES 1 TO 42

Cones 1–38, Mean of Data, Gas and Air
Average departure from mean (“gas” and “air”) 1.5°C

Rate °C/hr.	20	150		20	150	20	150
Cone No.	End point	End point	Diff. fast–slow	Bending interval	Bending interval	Cone interval	Cone interval
1	1125°C	1160°C	34°C*	30°C	45°C	10°C	5°C
2	1135	1165	28	30	45	10	5
3	1145	1170	25	30	40	20	20
4	1165	1190	26	40	35	15	15
5	1180	1205	28	40	50	10	25
6	1190	1230	39	40	35	20	20
7	1210	1250	43	40	60	15	10
8	1225	1260	35	45	55	25	25
9	1250	1285	32	65	115	10	20
10	1260	1305	44	40	95	25	20
11	1285	1325	36	70	80	25	10
12	1310	1335	27	80	45	40	15

*Values not rounded as in columns 2 and 3.

TABLE VI (*concluded*)

Rate °C/hr. Cone No.	20 End point	150 End point	Diff. fast–slow	20 Bending interval	150 Bending interval	20 Cone interval	150 Cone interval
13	1350	1350	− 3	70	55	40	50
14	1390	1400	8	100	70	20	35
15	1410	1435	26	85	115	40	30
16	1450	1465	16	70	125	15	10
17	1465	1475	7	50–75 ?	125	20	15
18	1485	1490	2	90	85	30	30
19	1515	1520	3	100	70	5	10
20	1520	1530	8	—	60		50
23		1580			30		15
26		1595			10		10
27		1605	Cones 23 to 38		15		10
28		1615	heated at 100°C per		10		25
29		1640	hour		30		10
30	In Arsem	1650			25		30
31	furnace at	1680			25		20
32	600°C	1700			15		45
33	per hr.	1745			30		15
34	1755	1760			15		25
35	1775	1785			15		25
36	1810	1810			25		10
37	1830	1820			5		15
38	1850	1835			15		
39	1865						
40	1885						
41	1970						
42	2015						

TABLE VII

END POINTS OF CONES 022 TO 01 (Heated in Furnace Gases)

Rate °C/Hr. Cone No.	20°C 10% CO_2	Diff. "gas"–"air"	150°C 10% CO_2	Diff. "gas"–"air"	Diff. fast–slow	20°C Cone interval
022	580°C	− 5°C*	—		—	20°C
021	600	+ 4	—		—	20
020	620	− 4	—		—	5
019	625	− 4				45
018	670	0	705°C	−11°C*	37°C*	40
017	710	− 6	760	−14	46	15
016	725	−10	780	−13	55	55
015	780	8	810	4	31	40
014	820	22	830	4	14	20
013	840	18	860	−1	17	55
012§	895	10	870	−8	−26	−5
011	890	16	905	+1	16	0

*Values not rounded as in columns 2 and 4.

§See foot note on page 715 regarding a second lot of cones 012, which were tested only in air. It is probable that the cones of this second lot would behave in a more nearly normal manner when heated in "10 % CO_2" than did those of the first lot.

TABLE VII (*concluded*)

Rate°C/Hr. Cone No.	20°C 5% CO_2	Diff. "gas"–"air"	150°C 5% CO_2	Diff. "gas"–"air"	150°C CO_2 10%	Diff. "gas"–"air"	Diff. fast–slow	20°C Cone interval
010	(890)[1]°C	(3)°C*	895°C	– 1°C*	895°C	–3°C*	(3)°C*	40°C
09	(930)[1]	(2)	935	5	945	17	(4)	45
08	975[2]	29	955	5	960	11	–18	25
07	1005	30	995	6	1000	14	–13	40
06	1040	35	1020	6	1035	19	–19	10
05	1050	20	1050	12	1050	11?	1	25
04	1075	22	1075	13	1085	23	1	25
03	1100	16	1115	– 1	1115	1	16	5
02	1105	10	1130	3	1130	3	23	10
01	1115	4	1150	1	1145	– 3	33	10

(1)3% CO_2
(2)955° in 3% CO_2
(3)5% CO_2

TABLE VIII

BEHAVIOR OF CONES 022 TO 4 HEATED IN FURNACE GASES FREE FROM SO_2

GAS ANAL. 10% CO_2

Cone No.	Rate of heating °C per hour	Bending	Bloating below end point	Surface action "skin effects"	Color	Remarks
022	20	fair	some	severe		OK
021	20	at base	severe	"		OK
020	20	" "	"	slight		OK
019	20	" "	none	slight		OK
	150	" "	severe	severe		NG
018	20	good	slight	slight		OK
	150	fair	very "	none		OK
017	20	normal	none	slight		OK
	150	fair	slight	none		OK
016	20	normal	none	none		OK
	20	"	"	"		OK
	20	"	"	"		OK
	150	fair	"	slight		OK
015	20	normal	"	none		OK
	20	"	"	"		OK
	20	"	"	"		OK
	150	fair	"	slight		OK
014	20	normal	"	none		OK
	150	fair	"	very slight		OK
013	20	normal	"	none		OK
	150	"	"	very slight		OK
	150	"	"	" "		OK
012	20	"	"	none		OK
	150	"	"	"		OK

Table VIII (*concluded*)

Cone No.	Rate of heating °C per hour	Bending	Bloating below end point	Surface action "skin effects"	Color	Remarks
011	20	"	"	"		OK
	150	"	"	none ?		OK
	150	"	"	"		OK
010	20	(stiff)	none	severe	—	NG
	150	at base[1]	some	"	—	fair
	150	" "	some	worse	green to brown[2]	fair
09	150	" "	none	severe	" " "	fair
	20	(stiff)	"	"	—	NG
08	150	at base	"	"	red-brown	fair
	20	(stiff)	"	"	" "	NG
07	150	at base	"	"	green-brown	fair
06	150	" "	"	"	brown	fair
05	150	" "	"	shows	red-brown	fair
04	150	" "	"	"	brown	fair
03	150	" "	"	slight	"	fair
02	150	" "	"	"	light brown	fair
01	150	fair	none	slight	light brown	fair
1	20	normal	"	none?	—	OK
	20	"	"	"	dark green	OK
	150	"	slight	none	gray	OK
2	20	"	none	none?	?	OK
	20	"	"	none	green-gray	OK
	150	"	slight	"	gray	OK
3	20	"	none	none?	?	OK
	20	"	"	none	light-gray	OK
	150	"	"	"	" "	OK
4	20	"	"	"	white	OK
	150	"	"	"	"	OK

OK = Data Used

[1] Cones 010 to 02 arched slightly, bent most at base

[2] Bloating broke skin. Inside of cone greenish

Table IX

Behavior of Cones 010 to 3 Heated in Furnace Gases free from SO_2

Gas Anal. 5% CO_2

Cone No.	Rate of heating °C per hour	Bending	Bloating	Surface action	Color	Remarks
010	150	(stiff)	some	severe	–	fair
	20[1]	at base	slight	"	green to brown	"
09	150	fair	"	some	red-brown	OK
	20[1]	at base	none		" "	fair
	20[1]	good	"	slight	brown	"
08	20	fair	slight	"	red-brown	OK
	20[1]	"	none	"	brown	OK
	150	normal	"	v. "	"	OK
07	20	fair	"	"	green to brown	OK

TABLE IX (*concluded*)

Cone No.	Rate of heating °C per hour	Bending	Bloating	Surface action	Color	Remarks
	20[1]	“	“	“	red-brown	OK
	150	normal	“	v. “	“ “	OK
06	20	good	“	v. “	“ “	OK
	150	normal	“	v. “	brown	OK
05	20	good	“	v. “	red-brown	OK
	150	at base	“	slight	“ “	NG
	150	normal	“	v. “	“ “	OK
	150	“	“	“	“ “	OK
04	20	at base	“	“	“ “	fair
	20	“ “	“	some	brown	NG
	150	normal	“	v. slight	“	OK
	150	“	“	“	“	OK
03	20	at base	“	some	“	fair
	150	normal	“	v. slight	“	OK
02	20	“	“	“	“	OK
	20	“	“	“	“	OK
	150	“	“	“	“	OK
01	20	“		“	light brown	OK
	150	“	“	“	“ “	OK
1	20	normal	“	v. “	light brown	OK
	20	“	“	“	“	OK
	20	“	“	“	“	OK
	150	“	“	none	“	OK
2	20	“	“	“	“	OK
	20	“	“	“	“	OK
	150	“	“	“	“	OK
3	20	“	“	“	“	OK
	20	“	“	“	“	OK

[1] CO_2 reduced to 3%.

TABLE X

BEHAVIOR OF TYPICAL CONES IN GASES CONTAINING SULPHUR OXIDES

Heating at 150°C/hr.			Gas anal. 5% CO_2, 0.35% SO_2		
Cone No.	End point	Effect on end point	Cone No.	End point	Effect on end point
017	760°C	*	02	1165°C	36°C
016	780	*	01	1175	27
015	820	+ 8°C	1	1180	15
			2	1180	20
011	900	− 4	3	1185	16
010	930	37	4	1200	11
09	950	16		10% CO_2 0.35% SO_2	
			18	1510	24
			19	1540	25
			20	1555	26

*Not run in 5% CO_2 free from SO_2

Would not "come down" in 10% CO_2 +0.35% SO_2

TABLE XI

DIFFERENCES OF OLD DATA FROM AUTHORS' RESULTS*

Cone No.	Original circular	1910 circular	Hofmann 1907–09	Hofmann 1911	Rieke 1911	Brown and Murray 1913	Fieldner, Hall, and Feild 1918
022	−15°C[1]	20°C[2]	[3]	[4]	15°C[5]	[6]	[7]
021	5	50			55		
020	0	50			50		
019	20	65			55		
018	−10	40			25		
017	−30	20			5		
016	−25	25			5		
015	− 5	10a			20a		
014	0	− 5a			−30a		
013	0	− 5a			−15a		
012	15	+ 5a			+ 5a		
011	15	−10a			5a		
010	55	0a			40a	0°C	
09	40	−10a			30	− 5	
08	40	−15a			45	10	
07	20	−40a			30	−35	
06	15	−60a			15	−45	25°C
05	10	−50a			30	−25	—
04	10	−55a			25	−30	25
03	−25	−60a			10	−45	—
02	−15	−45a			20	−40	55
01	−15	−35a			25	−35	—
1	−10	−25a			20	−40	20
2	5	−15a		− 5	15	−40	15
3	20	− 5a		5	10	−40	—
4	25	− 5a	45	0	− 5	−50	65
5	25	5a	25	—	− 5	−45	—
6	20	10a	35	—	−15	−50	55
7	20	20	40	−25	−20	−60	—
8	30	25	50	−20	0	−55	105
9	25	30	55	−20	5	−50	—
10	25	40	50	−15	0		30
11	25	35	45	—	0		40
12	35	40	50	—	0		
13	40	30	55	−25	−15		
14	10	20	25	− 5	−15		
15	−10	25	10	—	5		
16	−15	10	10	−40			
17	− 5	15	20	−50			
18	0	15	35				
19	− 5	5	25				
20	0	10	30				
23	10	—	10				
26	60	−10	20				
27	65	5	30				

TABLE XI (*concluded*)

Cone No.	Original circular	1910 circular	Hofmann 1907–09	Hofmann 1911	Rieke 1911	Brown and Murray 1913	Fielder, Hall. and Feild 1918
28	80	20	30				
29	70	10	30				
30	80	20	15				
31	70	10	30				
32	75	15	15				
33	45	−15	−25				
34	50	−10	−20				
35	45	−15	−25				
36	40	−20					
37	50	5					
38	55	15					
39		15					
40		35					
41		−10					
42		−15					

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*Comparisons are made with authors' results under conditions most nearly alike. Differences are caused by differences in cones themselves as made by different manufacturers, by conditions of heating, and by errors in temperature measurements.

a. The "a" series of cones.

[1] The original circular was a pretty fair guess. Differences from authors' results in air at 150°C per hour.

[2] Differences from authors' results in gas at 20°C per hour.

[3] Hoffman's data corrected for temperature scale. Data obtained by very rapid heating in air.

[4] Trials of a few cones in industrial kilns. Conditions not stated. Data corrected as in (3).

[5] Rieke used kilns fired with coal or wood, rate of heating controlled roughly. No data on atmosphere. Mean of results at different slow rates.

[6] First data on Orton cones. Fired slowly in kilns using natural gas. Data on four different rates erratic. Results have been averaged. No condition or temperature measurements accurately described.

[7] Heated very rapidly in air. Temperature measurements doubtful. Poor "black body" conditions.

TABLE XII

MELTING POINT OF CONE 35 AND KAOLIN

Authority	Year	Material	Melting point
Tonin. Zeit. Circular	1910	Zettlitz kaolin cone 35	1770°C
Hofman	1911	" " "	1760[1]
Kanolt	1912	English "	1745[2]
Bowen and Greig	1924	Synthetic $Al_2O_3.2SiO_2$	1790[3]
Authors	1925	Florida kaolin cone 35	1785[4]
"	1925	" " "	1775[5]

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[1] Very rapid heating in air

[2] Very rapid heating in vacuum, slightly reducing

[3] From equilibrium diagram for system Al_2O_3-SiO_2

[4] Heating 100°C/hr. in air

[5] Heating 600°C/hr. as in (2)

TABLE XIII

END POINTS AND INTERVALS OF PYROMETRIC CONES (Heated in Air)

Rate °C/hr. Cone No.	20°C End point	150°C End point	20°C Bending interval	150°C Bending interval	20°C Cone interval	150°C Cone interval
022	585°C	605°C	45°C	55°C	10°C	10°C
021	595	615	45	45	30	35
020	625	650	30	25	5	10
019	630	660	30	20	40	60
018	670	720	30	30	50	50
017	720	770	30	30	15	25
016	735	795	35	55	35	10
015	770	805	30	45	25	25
014	795	830	45	40	30	30
013	825	860	45	50	15	15
012	840	875	50	85	35	30
011	875	905	65	65	15	−10
010	890	895	30	25	40	35
09	930	930	35	40	15	20
08	945	950	55	60	30	40
07	975	990	35	50	30	25
06	1005	1015	25	35	25	25
05	1030	1040	30	30	20	20
04	1050	1060	40	40	30	55
03	1080	1115	40	35	15	10
02	1095	1125	35	35	15	20
01	1110	1145	50	45	15	15
1	1125	1160	30	45	10	5
2	1135	1165	30	45	10	5
3	1145	1170	30	40	20	20
4	1165	1190	40	35	15	15
5	1180	1205	40	50	10	25
6	1190	1230	40	35	20	20
7	1210	1250	40	60	15	10
8	1225	1260	45	55	25	25
9	1250	1285	65	115	10	20
10	1260	1305	40	95	25	20
11	1285	1325	70	80	25	10
12	1310	1335	80	45	40	15
13	1350	1350	70	55	40	50
14	1390	1400	100	70	20	35
15	1410	1435	85	115	40	30
16	1450	1465	70	125	15	10
17	1465	1475	50–75?	125	20	15
18	1485	1490	90	85	30	30
19	1515	1520	100	70	5	10
20	1520	1530	—	60		50

TABLE XIII (*concluded*)

Rate °C/hr. Cone No.	20°C End point	150°C End point	20°C Bending interval	150°C Bending interval	20°C Cone interval	150°C Cone interval
23	In Arsem furnace at 600°C per hr.	1580	Cones 23 to 38 heated at 100°C per hour	30		15
26		1595		10		10
27		1605		15		10
28		1615		10		25
29		1640		30		10
30		1650		25		30
31		1680		25		20
32		1700		15		45
33		1745		30		15
34	1755	1760		15		25
35	1775	1785		15		25
36	1810	1810		25		10
37	1830	1820		5		15
38	1850	1835		15		
39	1865					
40	1885					
41	1970					
42	2015					

The temperatures in the above table, which have been determined under standardized and reproducible conditions (controlled rate of heating in clean air) will apply with fair approximation for the cones when heated in kilns where the gases are normally oxidizing and free from sulphur oxides. If the cones show a visible hardening of the surface or a skin effect resulting from exposure to kiln gases containing insufficient oxygen, small corrections may be necessary. Such surface action is most frequently noticed with cones 015 to 01. In kilns fired with fuel containing appreciable amounts of sulphur, or where the ware gives off sulphur dioxide the end points may be noticeably different from those given in the table.

Discussion

H. B. HENDERSON: There is one very important factor in firing clay ware, in the behavior of cones in testing and in use, which has not been considered by the authors. This factor is the effect of absorbed or deposited carbon in ceramic products. All ceramic ware are effected, some detrimentally, but in others the effect is intentional because of the color value, as for example the russet color of salt-glazed products and flashed fire clay products.

It is well known that methane, the chief constituent of coal gas and natural gas, readily dissociates at temperatures above 800°C and that carbon is one of the resulting products. It is this element, in a nascent state, that is superficially absorbed by the ware or deposited on the surface with slight penetration into the ware. The dissociation appears to be a surface condition; *i.e.*, it seems to be at a maximum at the surface of red hot cones or clay ware. The carbon when deposited under these conditions is hard and lustrous and apparently graphitic, and it is more difficult to burn out than the soft sooty variety known as lamp black. This lustrous graphite carbon may sometimes be seen in coke surfaces, but the best examples are the "horns" of gas carbon that often build up in the throats of improperly fired natural gas furnaces, a hard, lustrous cone of carbon, infusible, and measurably non-combustible.

Cones are very seriously affected by such carbon deposits or absorptions as I have frequently seen in tests which have been sent into the laboratory for an explanation of their erratic behavior.

I reported[1] the first results of a series of observations on the effect of carbon on clay ware. Portions of the article were deleted by the editor and practically all reference to the effect of carbon was omitted. The editor graciously passed the statement that salt glazes contain carbon taken up as above outlined, and he permitted the further statement that the carbon, likely in the form of graphite, affects or influences crystal growth to which the color of salt glazes and flashed fire bricks is due, and in this line of ceramic products we have a notable example of the effects of carbon, a desirable effect because of the color and no harm to the ware itself.

In a number of factories, the dark russet color or a light straw color is developed at will by the method of firing and cooling. In the dark-colored product the firing conditions are strongly reducing and the carbon absorption is high, whereas in the light-colored product oxidizing conditions are maintained as fully as it is possible to do with the result of very low absorption. This has no bearing on the behavior of cones except as further evidence of the development and control of carbon in kiln gases and its absorption into the surface of the ware.

In various porcelain bodies the effect of the deposited carbon is very serious and it may entirely vitiate the value of pyrometric cones.

Figure 1 shows three pats of cones, in which are cones 9, 10, 11, all from the same boxes of cones, that is, the same batches. Plaques No. 1 and No. 2 were fired in a commercial kiln and were returned to the laboratory for an explanation of their erratic behavior. Plaque No. 3 was then fired in a test kiln.

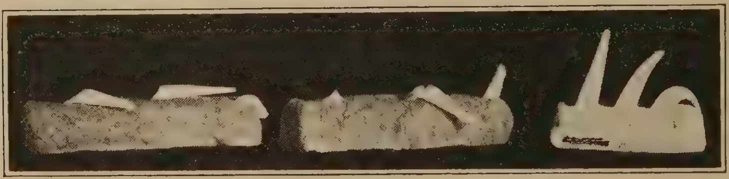

FIG. 1.

The cones on No. 1 and No. 2 have a hard, dry, lusterless surface showing that there has been no fusion, no softening of the surface shell, due to the fact that carbon has been absorbed and the shell made more refractory in consequence. The fireclay body in which the cones were set has a beautiful golden color such as is produced in fire-flashed brick.

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[1] *Jour. Amer. Ceram. Soc.*, **1**, 148–59 (1918).

Since the commercial kiln cones were being used as temperature guides and because they did not go over, the kiln temperatures were carried higher without affecting the refractory shell but the normal interior of the cones softened, became fluid, and ran out at the bottom forming a puddle of fused glass in which stood the refractory hollow cone shell, but it subsequently toppled over without bending and without having its edges rounded by fusion. Number 9 cone did not topple over but stood erect, merely settling down into the soft glass in the hold in the pat. The No. 3 pat shows the normal behavior of these cones when properly treated.

Bradshaw and Emery[1] reported an investigation demonstrating conclusively that methane dissociates in contact with the surface of cones under fire, and that carbon develops and is absorbed by the ware thus forming a refractory shell that may support the cone and hold it erect until the interior fuses and runs out at the base leaving the hollow shell. This in the white cones becomes dark gray in color due to the deposit of carbon.

Since their work included cones of English and German manufacture, it is evident that this behavior under certain firing conditions is not limited to cones of American manufacture.

The carbon develops under strongly reducing kiln conditions, weak draft, closed fires, and deep fuel beds, in other words the kiln atmospheres which the sewer pipe and flashed face brick manufacturers develop to produce the russet color effects, and it carbonizes the cone surfaces and makes their use of no value. Especially is this true if the cones are so placed that they get flame contact.

It is too common a practice to place cones on a ledge of ware in the wicket space, where the gases immediately from the bags are reducing in spite of their air excess, and where the cones are bathed in flaming gases with each firing, and where they become coated with ash dust. Under such conditions cones cannot function properly. In any instance where the cones do not bend normally, where the edges do not soften and become rounded, the firing conditions are at fault.

EDWARD SCHRAMM: A word of appreciation should be given to Dr. Fairchild for this careful investigation of pyrometric cones and especially to the general conclusion that cones are essentially temperature measuring devices. A cone will come down over a range of temperatures depending on the firing curve followed, but under these circumstances identical cone indications do not mean the same thing since it is only rarely and by accident that the work can have the same thermal characteristics as the cone. The best procedure, therefore, is to take care of the time by means of a clock, *i.e.*, to follow a definite time-temperature curve, in which case, as shown by Dr. Fairchild, the cones are quite satisfactory for the measurement of temperatures. There will be quite a variation in the temperature indicated by a given cone from plant to plant, but in spite of that it would be possible to devise a cone-temperature scale for average conditions which would fit a large number of cases. If we were starting anew, it might be best to avoid such a scale; but there is actually current, or at least printed in all books on ceramics, an erroneous scale dating back to Seger and sedulously copied ever since. It would do no harm to get out a new scale which would come a little nearer the truth.

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[1] *Trans. Ceram. Soc.* (Eng.), **21** [2], 117 (1922).

If cones are merely for the measurement of temperatures we might ask why not dispense with them and use thermocouples. It is entirely a matter of convenience. Cones can be distributed throughout a kiln in a manner not feasible with thermocouples.

I do not agree that the cones cannot be used for measuring the rate of heating. A kiln can be operated so as to bring down successive cones in definite intervals of time and so we can come quite near to following the same time-temperature curve by controlling the rate at which the cones come down.

F. H. Riddle: It is rather hard for me to agree with what Dr. Schramm has said about the difference in temperature in rapid and slow fire. I have taken the average of cones to about 9 and the difference in temperature on the end point is on an average of 15°, and the variations in temperature of the end point 20–150°, and on 12 cones from 1 to 12, is 33°. These figures make it hard to agree with Dr. Schramm, for we have less variation between cone intervals by practically one-third than we have variations in temperature between the slow and rapid fire.

Careful inspection of the cones after the fire is necessary. If the cones are carefully inspected after the fire as to the amount of seed in them, and particularly those cones which are thoroughly fused, if they form a beautiful colored glass, or if they form a lot of seeds, it is a fine indication of just exactly what kind of firing you have had. Almost invariably, if the lower cones (cones 4 or 5), are below the measuring point, in a steady condition, the clays will be the same way. By adjusting it, there is a good control.

R. F. Geller: We had prepared one slide here to anticipate a logical question, namely: how close can you come to these temperatures in your own kiln, and what it all means to you practically. In our work to determine the relative softening points of foreign and American cones, we have followed a certain heating schedule, which entailed heating measurements. So, incidentally we determined also the temperature at which those cones softened under our conditions, which are not so far removed from plant conditions. (Here Mr. Geller presented a slide, showing certain figures covering an entire series of cones from 022 to 34, and explained the relation of these figures one to another with special reference to temperatures.)[1]

F. H. Riddle: When I was abroad, they were using cones in France. Cone 1380 would be cone 1.

H. B. Henderson: There are two series of cones from France. One is marked with the number of degrees centigrade at which it is supposed to melt, and the other one is numbered in the usual way. There is not much difference in these two series.

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[1] See "A Comparison of the Softening Points of some Foreign and American Pyrometric Cones," *This Jour.* p. 748

A COMPARISON OF THE SOFTENING POINTS OF SOME FOREIGN AND AMERICAN PYROMETRIC CONES[1]

By R. F. Geller and E. E. Pressler

ABSTRACT

This paper is a report of results obtained from a study of the softening points of pyrometric cones as made in England, France, Germany, and America. The results are briefly discussed and are also shown photographically so that interested readers can best obtain the specific information they desire from a study of these photographs. The data obtained further indicate that the temperature at which the cones most used in the trade (Nos. 1 to 20) soften can be determined with an accuracy of ±15°C in laboratory kilns of the gas-fired type, provided good pyrometric equipment is used and reasonable precautions are taken to maintain definite rates of heating. Errors of as much as ±25° can be expected in the determination of temperatures at which cones less refractory than No. 1 or more refractory than No. 20 soften. In the case of more refractory cones this is due principally to the difficulty of maintaining definite rates of heating while, in the case of the less refractory cones Nos. 022 to 01 inclusive, inaccuracies can be attributed both to difficulty of maintaining definite heating rates and to the sensitiveness of the softening behavior of the cones to furnace atmospheres. This is particularly true of the "red series" (cones 010 to 01) the softening points of which are materially affected by changes of a few per cent in the CO_2 and SO_2 content of furnace gases.

Purpose

The immediate purpose of this investigation was to compare the softening points of representative foreign and American cones under conditions of temperature uniformity and rates of heating known and controlled within limits practical for the average laboratory, but with the determination of the softening points (expressed in temperature) as an incidental factor. It was thought that this information would serve a useful purpose for those investigators who wish to interpret data expressed in cones and contained in European literature.

Cones Used

Cones of American (Standard Pyrometric Cone Co.), English (Central School of Science and Technology), German (Royal Porcelain Co.), and French (Paulene Freres) manufacture were used in this investigation. They were obtained by Edward Orton, Jr., and are believed to represent the cones most used in the particular country represented. Necessary precautions were taken to obtain specimens typical of the product as supplied to the industry.

Scope

The cones investigated ranged from Nos. 022 to 35, inclusive. Temperature readings were taken, but only insofar as necessary

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[1] Published by permission of the Director, Bureau of Standards, U. S. Department fo Commerce. Received September 7, 1926.

to maintain a predetermined rate of heating in the immediate vicinity of the cone pat under observation.

Method of Testing

A. Cones 022 to 20 The softening points of cones, ranging from No. 022 to No. 20, were compared in a gas-fired, recuperative type, semimuffle kiln. Figure 1 shows a cross-section of the kiln and the "setting" employed. Natural draft burners are placed at *B* (Fig. 1) and the air for combustion (preheated by the outgoing gases) rises through ports at *A*. The burning gases are drawn up and over the bag walls and then down around and under the muffle, containing the cones, to chamber *C* of the recuperator. Although the flue gases were not analyzed, it is fairly certain that a neutral or oxidizing furnace atmosphere was maintained at all times. The fuel used was carbureted water gas of the following approximate composition, given in per cent: CO_2, 5; O_2, 1; CO, 25; H_2, 34; CH_4, 15; illuminants, 12; H (by difference), 8; the average heating value is 600 B.t.u. per cubic foot.

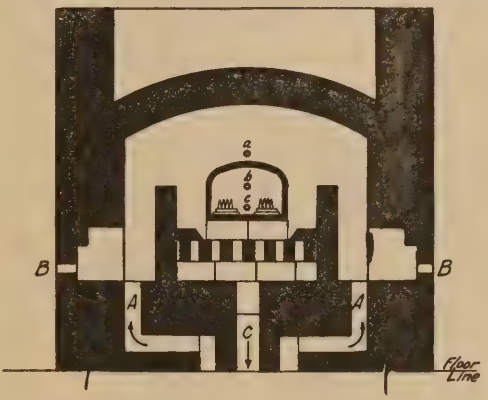

FIG. 1.—Indicates setting of gas-fired, recuperative, downdraft kiln in which the comparative softening points of cones 022 to 20 were determined.

Each plaque carried four cones of one number (English, French, German, and Orton), the height of the plaque, the depth to which the cones were embedded,[1] and the angle of inclination (8°) being maintained practically constant in all cases by means of the gage shown in Fig. 2. In placing the plaques in the muffle they were set level in order that the angle of inclination of all cones might be the same at the beginning of the test.

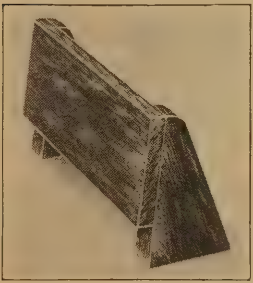

FIG. 2.—Gage used in setting cones at inclination of approximately 8°

The cone plaques (mixtures of calcined Al_2O_3 and kaolin) were placed within a secondary muffle (Fig. 1) and all plaques were tested in duplicate. Furthermore, they were so placed that the positions of the respective cones in the one plaque, relative to the distance from the muffle wall, were reversed in the duplicate plaque. This was done to reduce the errors caused by temperature gradients within the muffle. Tested duplicate plaques indicated that the error from this source was negligible.

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[1] By embedding all cones to the same depth, the results include variations due to differences in the overall lengths of the cones and the consequent variations in the height to which they would normally protrude above the pat.

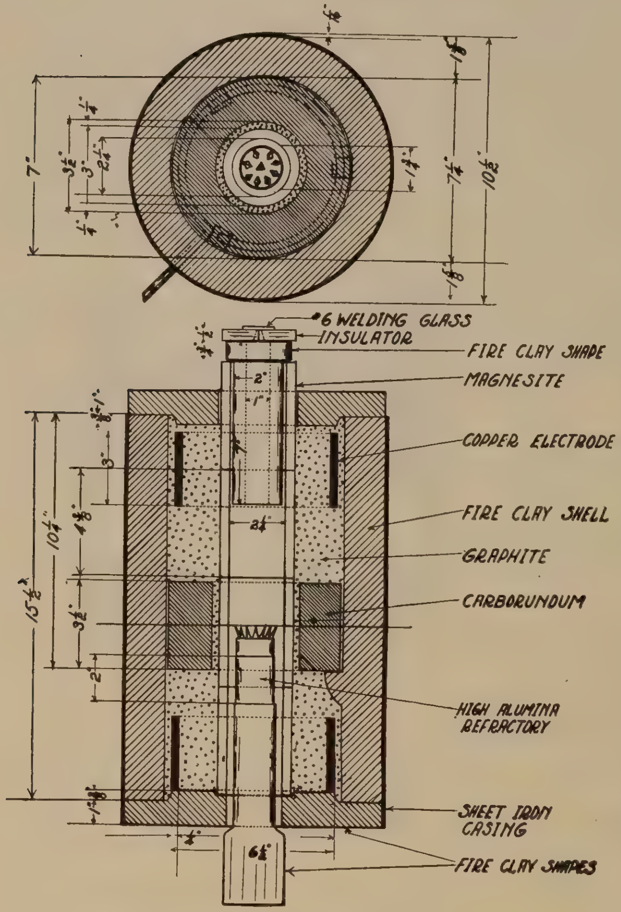

Fig. 3.—Sketch of graphite resistance furnace used in determining the comparative softening points of cones 26 to 35. (For detailed information see paper by W. L. Pendergast, *Jour. Amer. Ceram. Soc.*, **8** [5], 319 (1925).

The muffle accommodated ten plaques (representing cones of five numbers). The plaques were placed with the cones in numerical order, the one of lowest number being in front where it could be most conveniently withdrawn at the proper time.

Rate of Heating The temperature was raised at the rate of 50°C per hour to within 300°C of the temperature (as given by the maker) of the American cone of lowest number in the muffle. Thereupon the rate was changed to 20°C per hour and maintained until the completion of the test.

Each pat was withdrawn as quickly as possible when the tip of the American cone was level with the top of the plaque.

B. Cones 26 to 35 The softening points of the small cones (26 to 35) were determined in the electrically heated furnace shown in Fig. 3.

A plaque of four cones was used, the same precautions of setting being observed as for the larger cones. However, four cones of one number were not placed in one plaque. Instead, American cones were used of lower and higher number than the foreign cone to be tested. In this way a direct comparison of one foreign cone with the American cones of higher and lower softening points is obtained, rather than a direct comparison of the four types of one number.

This procedure was followed because of the relatively large differences found, particularly for cones 26, 27, and 28.[1]

Plaques 4, 5, and 6 (Fig. 15) illustrate the steps required to obtain a desired comparison. The range of American cones was lowered, in this case, until the cone of approximately the same softening point as the French cone was found.

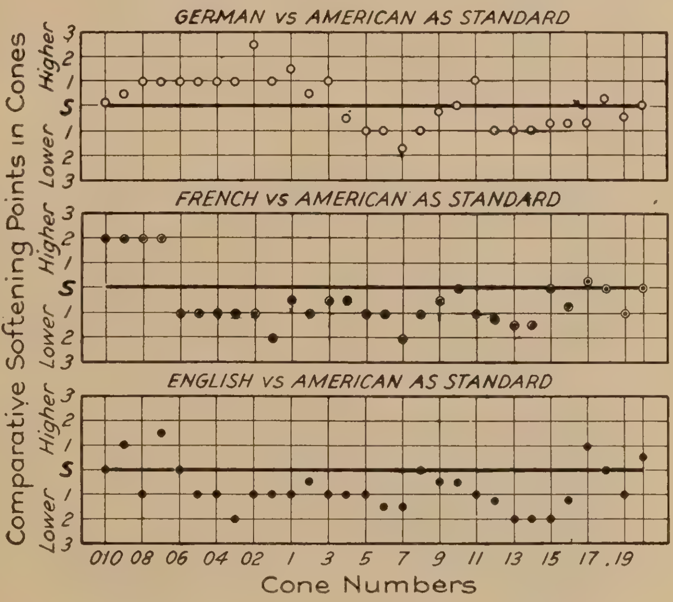

FIG. 4.—A graphic method of representing comparative softening points.

Rate of Heating The plaques of cones 26 to 35, which were tested in the electrically heated furnace, were precalcined in a gas-fired furnace at 1000°C. Between softening point determinations the temperature of the electric furnace was permitted to drop to approximately 1000°C, a calcined cone plaque was inserted, and the temperature from this point raised according to the rate specified in the A.S.T.M. Standard Method of Test for Softening Point, Serial Designation C 24–20.

Method of Presentation

Several methods of presenting the results were tried in an endeavor to enable the reader to gain quickly a comprehensive idea of their nature.

A. In Fig. 4 a straight line was drawn as a base line representing the softening points of the American cones 010 to 20. A comparison was then obtained by plotting the relative softening points of the German, French, and English cones at the proper intervals (expressed in cones) above or below the line, depending on whether they were more or less refractory than the American cone of corresponding number.

B. Drawings were made of the entire series as shown in Fig. 5.

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[1] It would have been advisable to follow such a procedure with the cones of lower number, but this would have required more time than was available for the investigation.

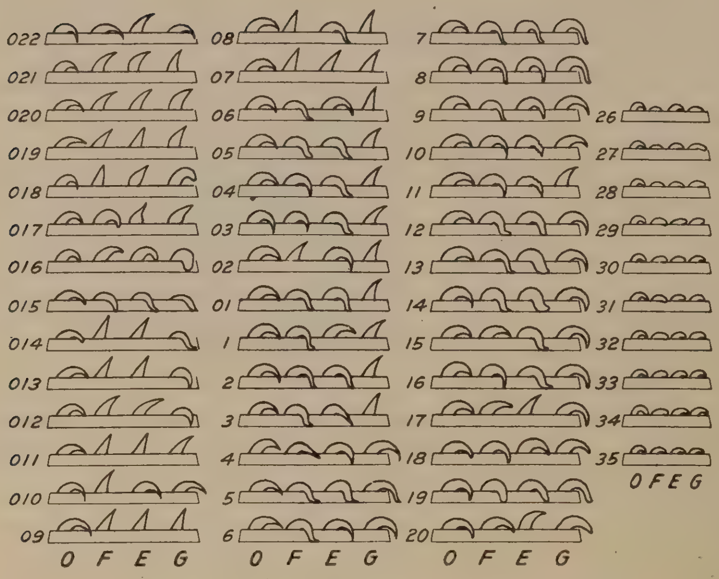

FIG. 5.—The entire series of cones sketched to give a concise representation of comparative softening points.

This is a simple and compact presentation, probably serving its intended purpose. However, it is believed that the user of cones would prefer his own interpretation based on the appearance of the cones themselves. For this reason a photograph of a typical plaque is given for cones of each number.

Results

A. The Hecht Series, Cones 022-011 (Figs. 6 and 7.) The cones of this series are colored as shown in Table I.

TABLE I

COLORS OF CONES BEFORE FIRING

Cone	Orton	German	French	English
022	White	Buff	Buff	Light gray
021	Buff	“	Gray	“ “
020	White	Old rose	Yellow	White
019	“	White	White	“
018	“	Old rose	Buff	“
017	“	“ “	Yellow	“
016	“	Pale green	White	“
015	“	Buff	“	“
014	“	Old rose	Green	“
013	“	Gray	White	“
012	“	Buff	Buff	“
011	Buff	Old rose	Gray	“

The results for cones 022 to 016 inclusive cannot be compared satisfactorily, due to the "bloating" of many of the foreign cones under the conditions of the tests. For example, English cones 021, 018, and 017 have been bent over by bloating at the base; the same is true of German cones 020, 018, and 017. All of the cones of foreign make from 022 to 017 tended to become vesicular in structure and were extremely sensitive to temperature change, causing them to break into two or more pieces on removal from the kiln. For photographing it was necessary to glue these pieces in place.

The results may be generalized as follows:

German cones 022, 018, 015, 014, 013, and 012 were from one to two cones softer (*i.e.*, less refractory) than the American, while cones 021, 020, 019, 017, 016, and 011 were one or more cones harder (*i.e.*, more refractory).[1]

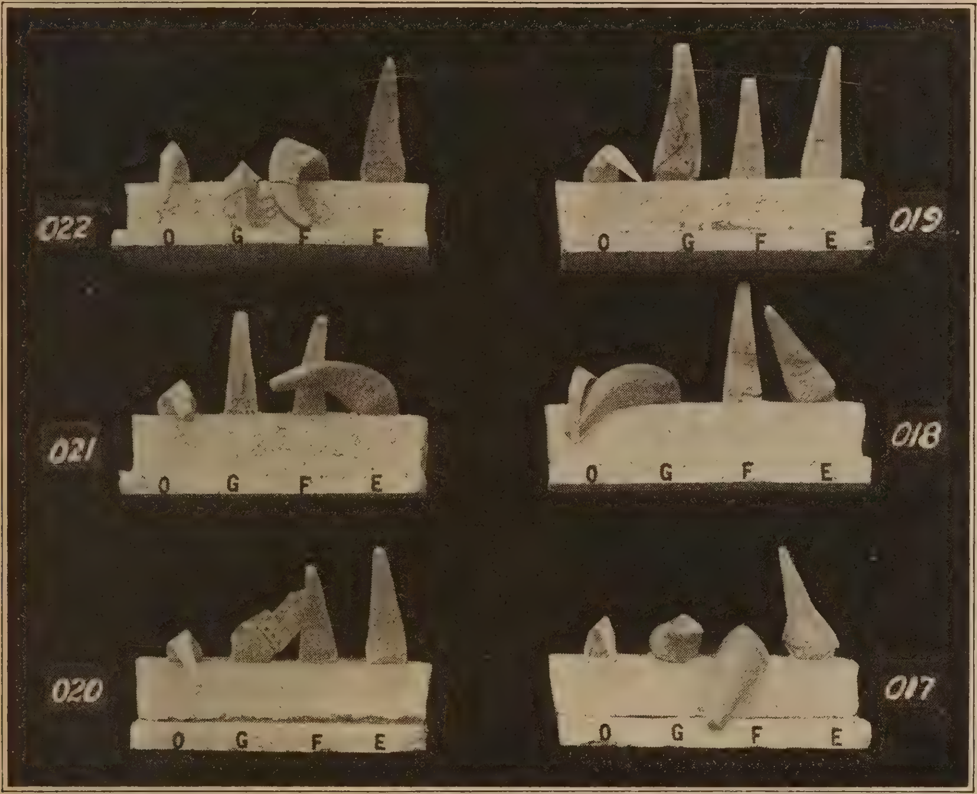

Fig. 6.—Photographs of typical pats showing softening points of cones 022 to 017. O: American; G: German, F: French; E: English.

French cones 022, 017, and 015 were softer by one cone or less, while the balance of the series were harder by, apparently, from 1 to 3 cones.

All of the English cones (with the exception of 015 and 012) were harder, practically paralleling the French series.

B. The Cremer Series, Cones 010-01 (Figs. 8 and 9.) The American and German cones of this

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[1] The temperature interval represented by "1 cone" will vary. For data regarding those of the American cones see C. O. Fairchild and M. F. Peters, "Characteristics of Pyrometric Cones," *This Jour.*, p. 701–43. These data will serve to illustrate the differences in cone intervals and also in bending intervals. Furthermore, the cone and bending intervals of the foreign cones may be quite different from those of the American cones and, therefore, "cone differences" can be at best only rough approximations.

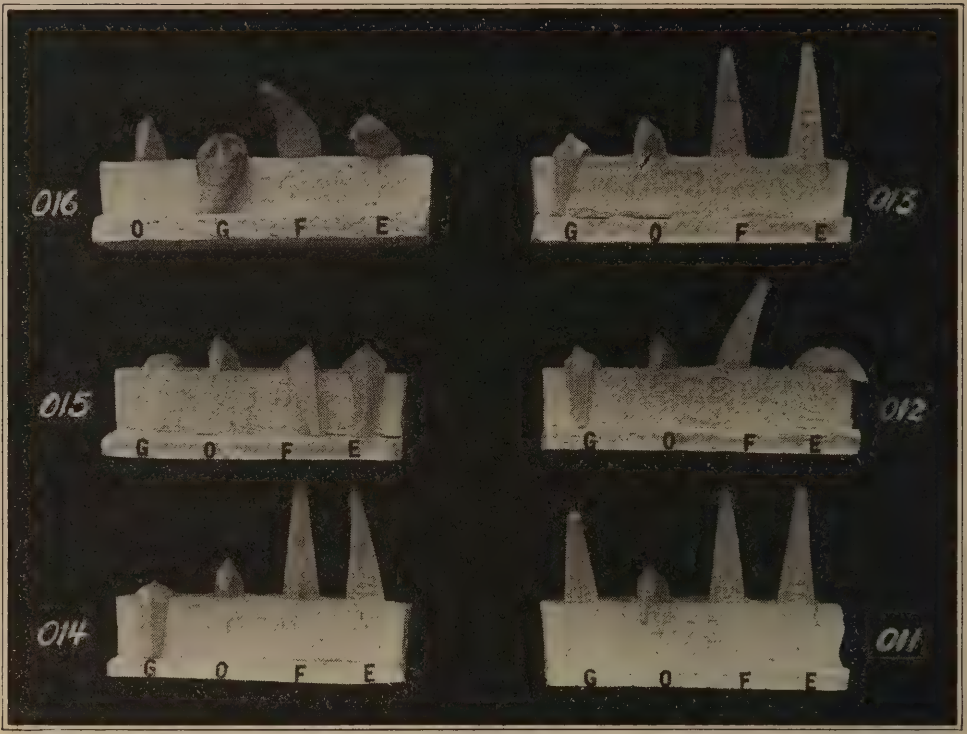

FIG. 7.—Photographs of typical pats showing softening points of cones 016 to 011. O: American; G: German; F: French; E: English.

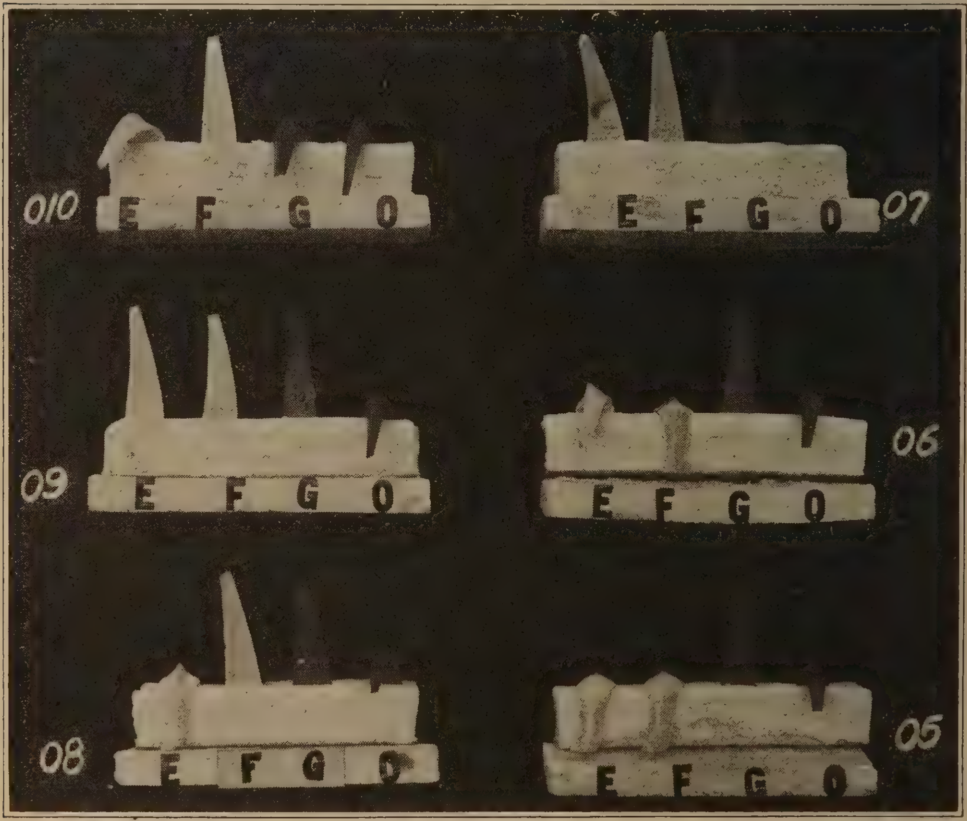

FIG. 8—Photographs of typical pats showing softening points of cones 010 to 05. O: American; G: German; F: French; E: English.

series are red, the French are varicolored, and English are white (Table II).

TABLE II

COLORS OF CONES BEFORE FIRING

Cone	Orton	German	French	English
010	Red	Red	White	White
09	"	"	"	Gray
08	"	"	Old rose	White
07	"	"	Green	"
06	"	"	Old rose	"
05	"	"	Green	"
04	"	"	White	"
03	"	"	Green	"
02	"	"	Lavender	"
01	"	"	Green	"
1	"	"	Light gray	"

With the exception of English and French cones 04, 03, 02, and 01 (Fig. 9), this series softened and bent normally. Each of these four

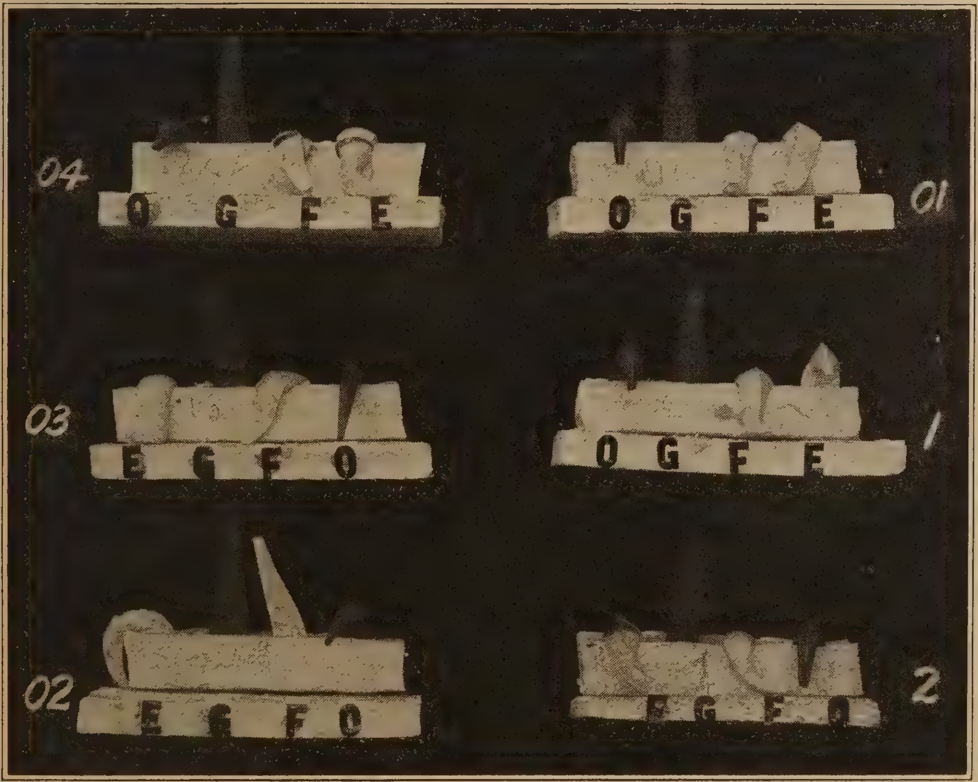

FIG. 9.—Photographs of typical pats showing softening points of cones 04 to 2. O: American; G: German; F: French; E: English.

cones formed a refractory "skin" which had a tendency to hold the cone upright after the interior had become quite soft. It should be noted that American cones 010, 09, and 03 passed the "end point" (described at the end of part A under Method of Testing, p. 745) while being removed from the muffle.

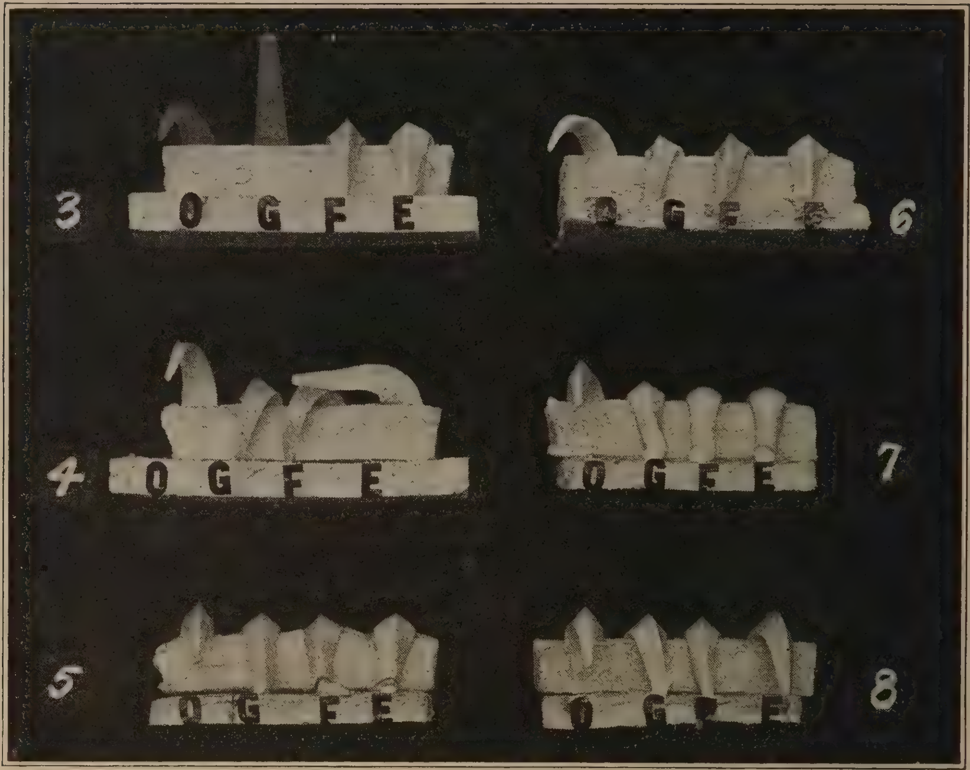

FIG. 10.—Photographs of typical pats showing softening points of cones 3 to 8. O: American; G: German; F: French; E: English.

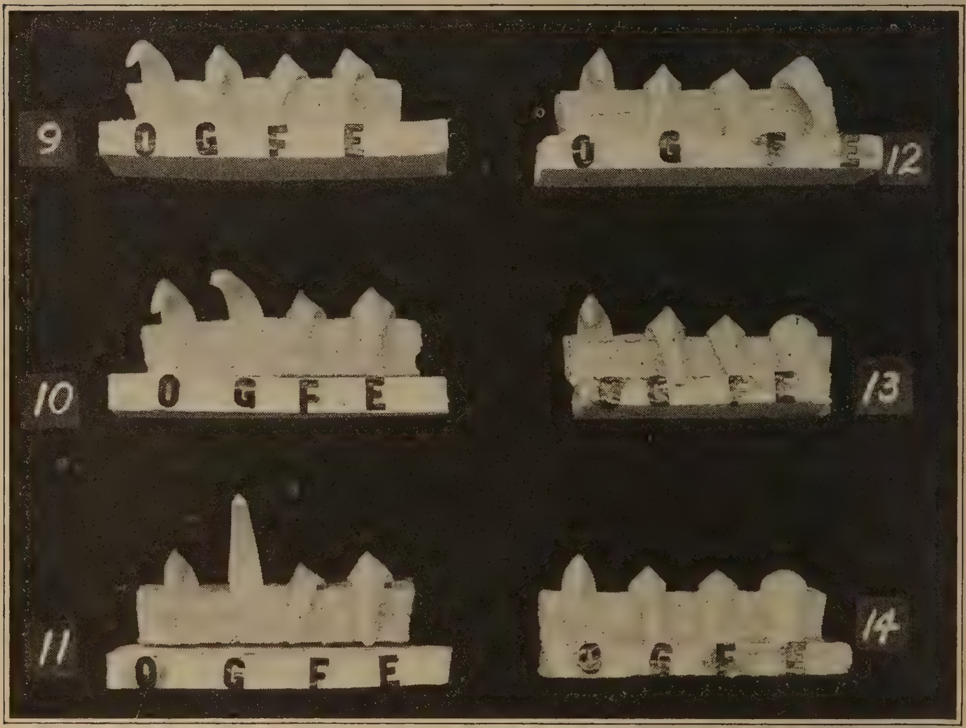

FIG. 11.—Photographs of typical pats showing softening points of cones 9 to 14. O: American; G: German; F: French; E: English.

German cone 010 was approximately the same as the American cone of the same number, but all the others of the series were harder by what appeared to be at least one cone interval.

French cones 010, 09, 08, and 07 are harder than the American by one to two cones. At this point a marked change must have been made in the composition of one of the series, for the balance of the French cones are *softer* than the American by at least one cone.

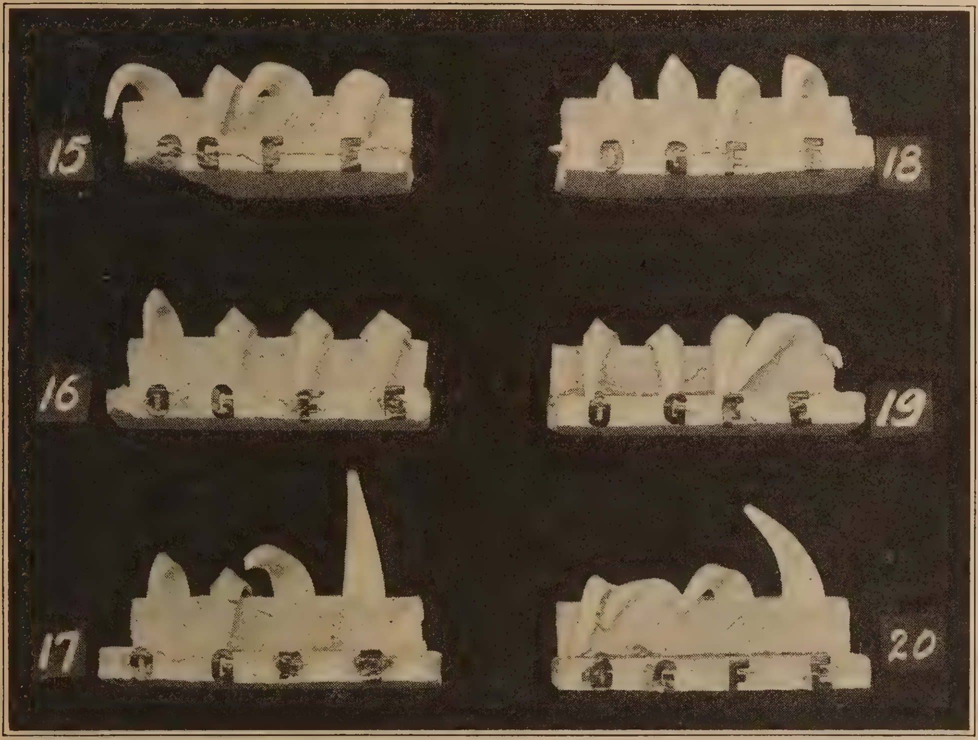

Fig. 12.—Photographs of typical pats showing softening points of cones 15 to 20. O: American; G: German; F: French; E: English.

The behavior of the English cones 010 to 06 inclusive is somewhat erratic as compared with the American; cones 010 and 06 are approximately the same, 09 is at least one cone harder, 08 is about one cone softer, and 07 about two cones harder. For the balance of the series they are apparently about one cone softer.

C. The Seger Series, Cones 1 to 20, Inclusive (Figs. 9 to 12.) The cones of this series are colored as shown in Table III. After fusion all the cones are practically white with the exception of the American and German cones 1, 2, and 3, which are reddish brown, and the French cone 4 which is light blue.

(Note: while French cone 02 is still standing, it is believed that this is due to the "skin" formation previously mentioned.)

TABLE III

COLORS OF CONES BEFORE FIRING

Cone	Orton	German	French	English
1	Red	Red	Light gray	White
2	“	Buff	Gray	“
3	“	Red	Buff	Gray
4	White	Gray	Blue	White
5	“	Buff	White	“
6	“	“	“	“
7	“	“	“	“
8	“	“	Green	“
9	“	Gray	“	“
10	“	White	“	“
11	“	“	White	Gray
12	“	Buff	Gray	White
13	“	Light gray	Buff	“
14	“	Buff	Green	“
15	“	Light gray	Old rose	“
16	“	“ “	“ “	Gray
17	“	White	Green	White
18	“	Buff	“	“
19	“	White	Buff	“
20	“	“	White	Gray

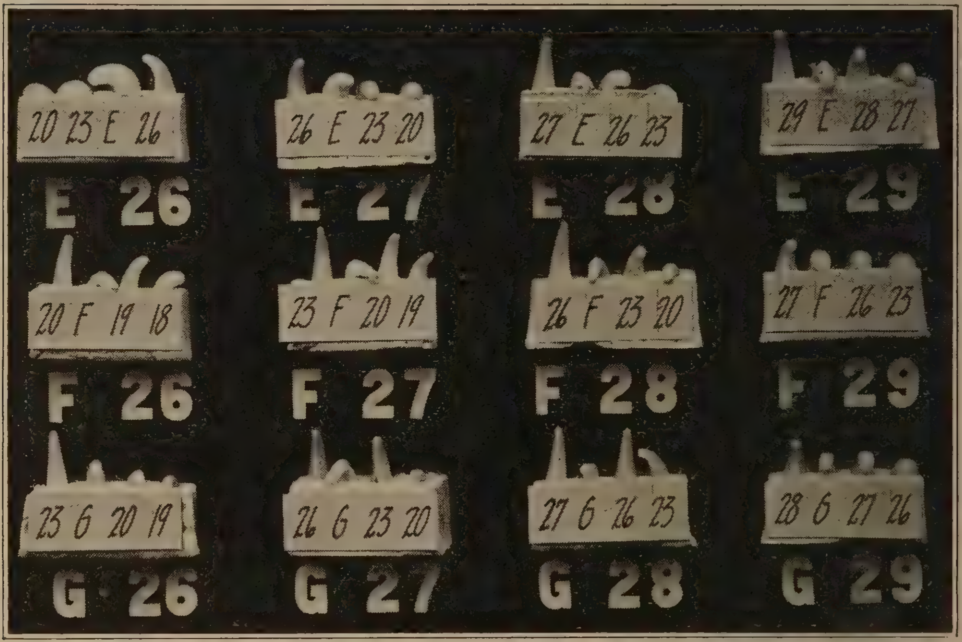

FIG. 13.—Photographs of typical pats showing softening points of cones 26 to 29. G: German; F: French; E: English; the cones referred to on the pats by number are American cones.

English cones 10 to 19 inclusive were found to bloat and blister, this being particularly true of numbers 13, 14, and 15. All others softened and bent normally; the peculiar behavior of English cone 4 in the plaque photographed is not typical. American cones 2, 8, 14, 18, 19, and 20 had passed the end point before they could be removed; this was due to the comparatively rapid bending of these cones with constantly rising temperature, and to the effects of the slight jarring incidental to their removal.

German cones 1, 2, and 3 are about one cone harder than the American, cones 4 to 8 from one-half to one and one-half cones softer, 9 and 10 appear to be practically the same, cone 11 is harder, cones 12 to 17 are consistently softer by about one cone and 18, 19, and 20 are the same as the American.

D. The High Temperature Series, Cones 26 to 35[1]

(Figs. 13 to 15.) All the cones in this series are white or a very light gray and all of the cones of foreign make are less refractory than the American, and markedly so in the case of cones 26 to 30.

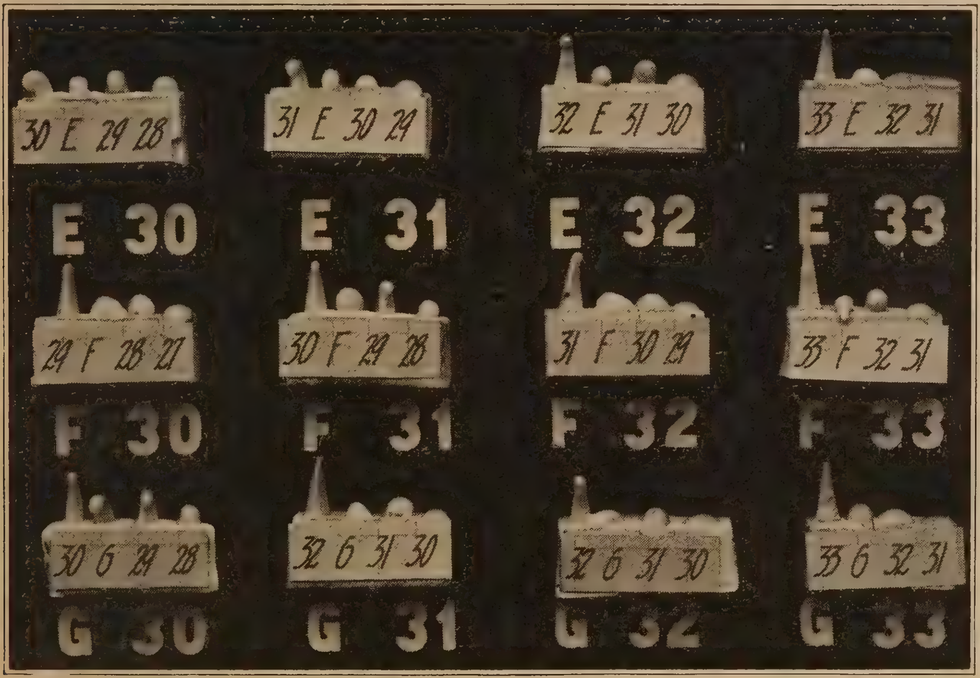

FIG. 14.—Photographs of typical pats showing softening points of cones 30 to 33. G: German; F: French; E: English; the cones referred to on the pats by number are American cones.

The greatest inconsistency noticed in the investigation was in the behavior of French cone 26. This cone is not only much softer than French cone 20 (plaques 2 and 3, Fig. 15), but it apparently has no definite softening point. In Fig. 13 it appears slightly softer than American cone 18, in plaque 2 (Fig. 15) it appears equal to the American

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[1] The entire series is composed of cones 26 to 42, inclusive; cone 35 was the highest numbered cone investigated.

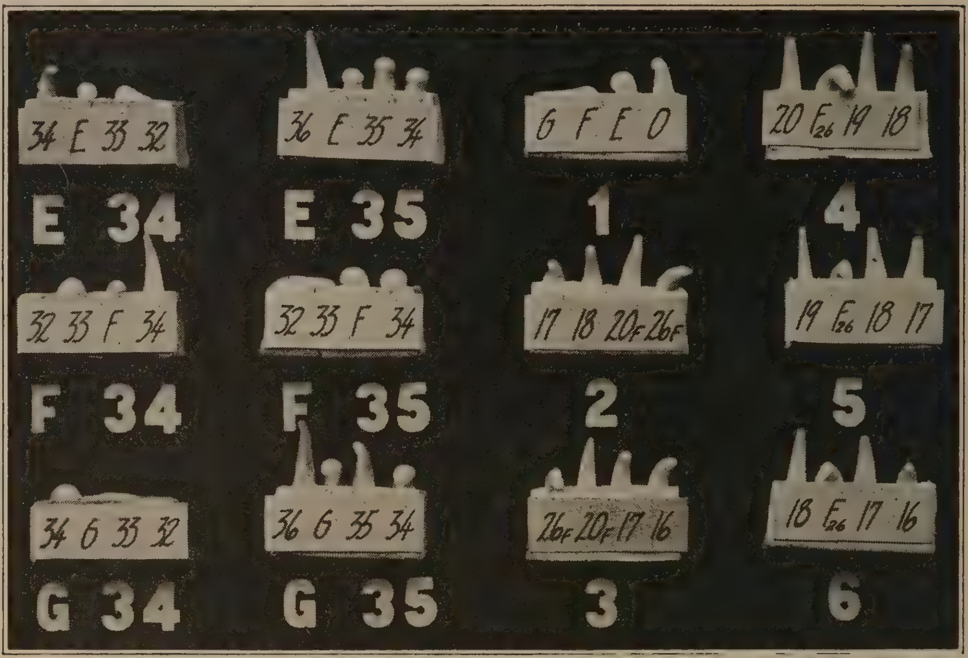

FIG. 15.—Photographs of typical pats showing softening points of cones 34 and 35. G: German; F: French; E: English; the cones referred to on the pats by number are American cones.

For comparison, cone 34 of each brand is shown in pat No. 1.

Pats 2 and 3 show French small cone 26 compared with French large cone 20 (cut down to the size of the small cone) and American cones 16, 17, and 18.

Pats 4, 5, and 6 illustrate the method used in determining the comparative softening points of the foreign cones 26 to 35.

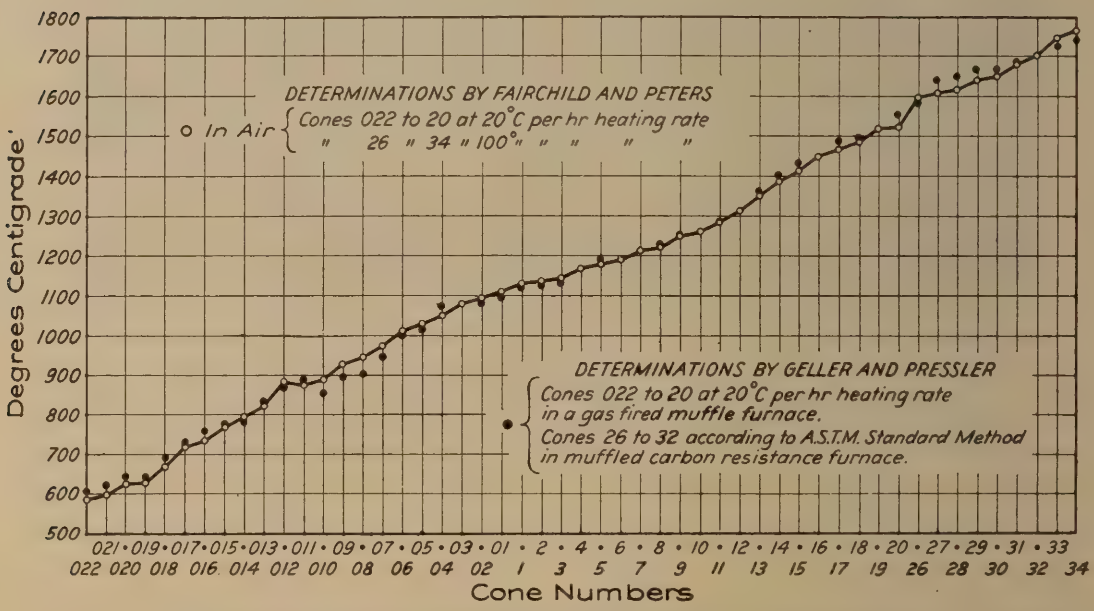

FIG. 16.—The temperatures at which American cones reached their end point, as determined in this investigation, compared with the more accurate determinations of Fairchild and Peters. (*This Jour.*, pp. 701-43.)

cone 17, and in plaques 3 and 6 (Fig. 15) it appears slightly softer than American cone 16. For convenience the results of this series are summarized in Table IV.

TABLE IV

The numbers in columns 2, 3, and 4 designate the American cone or cones estimated to be nearest in softening point to the foreign cone indicated in name by the column headings, and in number by column one.

(1) Cone	(2) German	(3) French	(4) English
26	20–23	(*a*)	23–26
27	20–23	18	23–26
28	23–26	20	26
29	27	26–27	27
30	29	27–28	28
31	30–31	28	30–31
32	31	29–30	31
33	32–33	31–32	32
34	33–34	32–33	33
35 (*b*)	34	34	34

(*a*) Discussed in Text.

(*b*) Results are not considered satisfactory, due to the "beading" of the cone, but are given as rough approximations.

Temperature and Time vs. Softening Point

The results shown graphically in Fig. 16 were recorded as a part of the investigation described above and are compared with determinations made under accurately controlled conditions.[1]

The data indicate that the temperature at which the cones most used in the trade (Nos. 1 to 20) soften can be determined with an accuracy of ±15°C in laboratory kilns of the gas-fired type, provided good pyrometric equipment is used and reasonable precautions are taken to maintain definite rates of heating. Errors of as much as ±25° can be expected in the determination of temperatures at which cones less refractory than No. 1 or more refractory than No. 20 soften. In the case of the more refractory cones this is due not only to greater errors of temperature measurements but also to the difficulty of maintaining definite rates of heating, while, in the case of the less refractory cones (Nos. 022 to 01 inclusive), inaccuracies can be attributed both to difficulty of maintaining definite heating rates and to the sensitiveness of the cones to furnace atmospheres. This is particularly true of the "red series" (cones 010 to 01) the softening points of which are materially affected by changes of a few per cent in the CO_2 and SO_2 content of furnace gases.

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[1] See Fairchild and Peters.

SILICON-CARBIDE REFRACTORIES FOR WATER-GAS GENERATORS[1]

By M. L. Hartmann[2] and John A. King[3]

ABSTRACT

A discussion of the problems involved in water-gas generator refractories is given and the steps in the development leading to the present highly satisfactory silicon-carbide air-ventilated Bernitz type blocks are given. Actual operating costs of typical installations are given. It is shown that generator capacities have been increased as much as 50% and fuel reductions have been so large that a real saving in net operating costs has resulted from the installation of this type of lining. Many generators have now been lined and economically operated with air ventilated silicon-carbide blocks.

The recognition of the cause of failure of refractories is frequently the longest step toward solution of the difficulty. So it has been with water-gas generators, although the complete solution was not attained in a single step.

Operators of water-gas generators have for years been struggling with clay linings. They have accepted frequent relining as a necessary evil, continually changing and experimenting in the hope of finding a miraculous clay or silica brick which would be almost permanent. To date no low (first) cost refractory materials have been found which give continuous and satisfactory service life.

How does a water-gas generator lining fail? Every observing operator knows that the usual clay linings are broken up by the incessant barring off of clinkers and ash which have fused to the clay blocks. Some grades of coal are worse than others. It is common practice to "bar down" generators twice a day, requiring three men from thirty to ninety minutes with a heavy bar rigged on a chain fall. The men must work from the top of the open generator, the heat is intense, the work heavy, and workmen cannot be expected to be gentle with the lining. In hammering off these clinkers, large pieces of the brickwork are broken out with the result that a good clay lining will last only about 1000 gas-making hours.

One of the first and most successful applications of silicon-carbide refractories was in boiler furnaces where their success was largely due to non-adherence of the clinker to the Carborundum. Similar results, logically, were expected in gas-generator linings. This proved to be true, but other factors offset this advantage to some extent, and the development was slow.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb. 1926. (Refractories Division.) Received Jan. 18, 1926.

[2] Director of Research, The Carborundum Co., Niagara Falls, N. Y.

[3] District Refractory Representative, The Carborundum Company, Worcester, Mass.

Plain Silicon-Carbide Linings

One of the early installations was made in a 9-foot water-gas generator set at New Bedford, Mass., in 1918. The blocks were of the type formerly manufactured by the Didier March Company, consisting of a thin silicon-carbide section dovetailed into heavier clay block. Although lasting only a few months, this test proved that clinker trouble could practically be eliminated. No longer life was obtained than with the clay alone due to the mechanical structure of the blocks. The veneer of silicon carbide began to break off and once started, adjacent surfaces peeled off rapidly. This type of block construction was abandoned.

Another installation in the same plant consisted of 4½ inch thickness of recrystallized Carborundum bricks known as "Refrax." These bricks are entirely Carborundum, with no bonding material, the bricks being held together by the recrystallization of the silicon carbide in an electric furnace. "Refrax" brick are extremely refractory, not melting even up to a temperature of about 4000°F, at which temperature Carborundum decomposes. The bricks are, however, somewhat porous and allow gas penetration.

This lining of circle bricks of "Refrax" material was installed in an 11-foot UGI set at New Bedford in 1920. The lining, 4½ inches thick, extended to a point of 5 feet above the grates. Backing the Carborundum was 9½ inches of clay brick followed by 2½ inches of diatomaceous earth brick. The set was started in March, 1921, and after eight months continuous operation, the vertical seams in the steel shell of the generator opened up due to the growth of the lining. Temporary repairs were made and the set was operated until March 28, 1922, at which time it was shut down for relining. The "Refrax" lining had lasted 4123 gas-making hours. Clinker troubles were practically nil; the work required to clean the clinkers off was insignificant in comparison with the work of cleaning off of clay blocks. The swelling of the lining was the direct cause of the failure.

Results on this lining seemed to warrant further trial and in April, 1922, another lining made of "Carbofrax" brick was installed. "Carbofrax" is the trade name for bonded silicon-carbide bricks and these were especially made to withstand penetration of gases and consequent oxidation. This installation was very successful, lasting 6687 gas-making hours. The lining gradually wore down until it was too thin for further patching. Another lining of Carbofrax was installed in November, 1923, and this lining is still in use. Up to the present time it has given a total of 6900 gas-making hours.

Walter M. Russell of the Massachusetts Lighting Co., writing as chairman of the Sub-Committee on Refractories of the American

Gas Association[1] reports further in regard to these plain generator linings:

> We find that about a year after a Carborundum lining is installed the side clinker begins to stick tighter to the lining due to small cracks in the lining brick and cement between brick coming out, giving the clinker a better chance to stick and so taking more time to break down side clinker but not so much time as required with a clay lining. Before the lining gets to this condition two men with a light bar can break off the side clinker in about 15 minutes.
>
> The Carborundum arches and jamb brick at fire doors we find require more patching than the lining due to striking of clinker bars against them and using the edge of the jamb as a fulcrum for clinker bars when the set is being clinkered.
>
> We also find it necessary to leave some clinker at the fire doors to keep the doors cool as due to the shape and size of the door jamb brick the Sil-O-Cel between these brick and the shell is much less than at other points, which with the greater conductivity of the Carborundum brick will cause the door frames to get red hot if no clinker is left in the doors.

The New Bedford Gas Company, however, considered the installation as a whole to be very satisfactory, for not only did it save money on repairs, but in their case saved them the investment of an additional water-gas set, which would have been necessary had they been required to use the clay blocks which necessitated relining shutdowns after 1000 gas-making hours.

Similar results were obtained at an installation in Springfield, Mass., where a life of approximately 7,000 hours was given by the Carbofrax lining.

In another installation the clinker costs were reduced as much as 40% and the labor cost reduced 20% due to the decreased number of shutdowns. It has also been observed that the longer life of the generator lining has directly resulted in the longer life of the carbureter and the checker brick. Shutdowns for repairs had formerly been determined by the life of the generator lining, but with Carbofrax lining it is now determined by the condition of the checker brick, and results obtained from the machine. One user has estimated that in the operation for the first ten months' period the lining has paid for itself and is in condition for at least three or four months more of operation. This means a very considerable saving.

On these latter installations allowance has been made in the outer shell to care for the growth or swelling of the silicon-carbide lining. Between the outer shell and the fire brick, a 2-inch space filled with asbestos has been provided, and between the fire brick and the silicon-carbide lining a 2-inch space filled with blue clay which allows for the later expansion of the silicon-carbide lining.

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[1] Report of Water Gas Committee, 1925 Convention, American Gas Association.

Linings of these types have not been, in general, considered wholly satisfactory in performance or life, and are no longer recommended since the perfection of the Bernitz block lining.

Bernitz Block Linings

The newest and most successful development in this field is the Bernitz block lining. For a number of years the Bernitz Furnace Appliance Company has marketed an air-cooled block to prevent clinker adhesion. These had been extensively used in boiler furnaces and it was natural to expect them to prevent the same difficulty in water-gas generators.

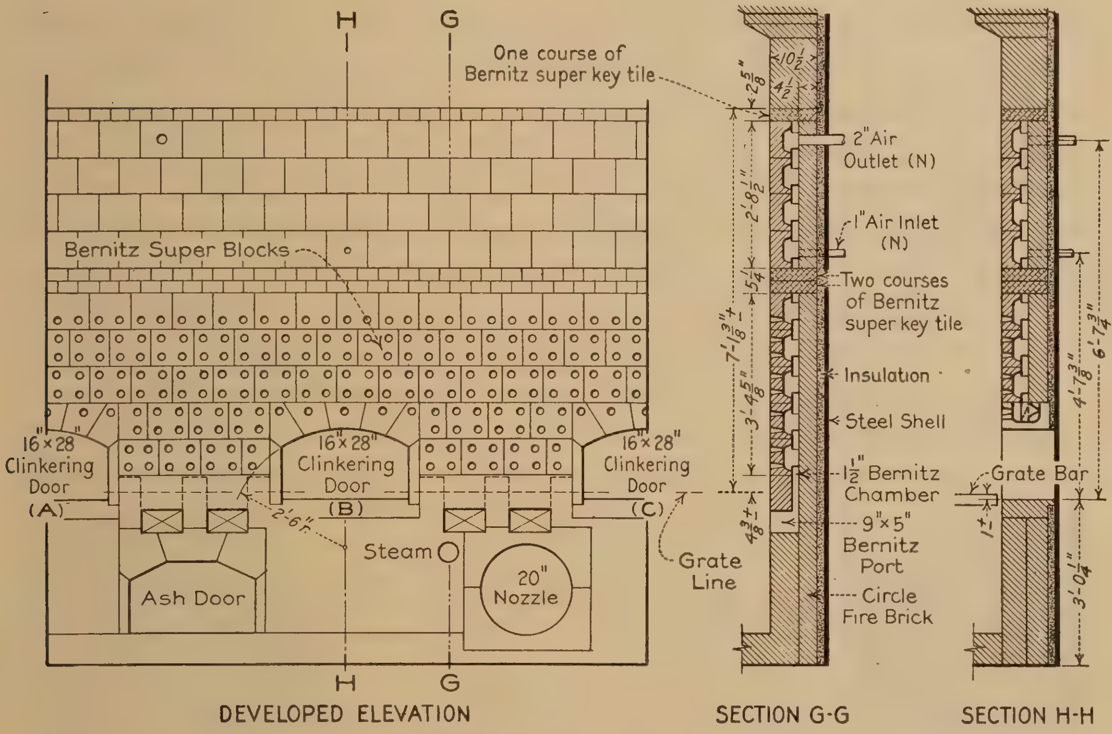

FIG. 1.

In May, 1922, an installation of fireclay Bernitz block was made in an 8-foot set at Gloucester, Mass. This trial, however, was not successful, the clay disintegrating by spalling. There was no apparent advantage in using the air-cooling system with clay-generator linings.

A big step in advance was made when Bernitz blocks made of Carbofrax were adopted for preventing clinker adhesion and slag erosion in boiler furnace practice where their almost universal success naturally lead to their trial in water-gas generators.

A typical Bernitz block is shown in Figs. 2a and 2b. The hollow block shape is pierced on the side adjacent to the fire with a number of cone-shaped holes larger at the face and smaller at the back. When used as a lining for water-gas generators these holes permit the introduction of the air or steam at various points in the fire. The great mechanical strength of Carbofrax at high temperatures, its lack of chemical activity in contact with chilled or viscous slags, and the high thermal conductivity which permits sufficient cooling of the working surface to prevent reaction with and adherence of slags, are the reasons for its remarkable success in water-gas linings.

A number of successful installations have been made during the past two years. Certain improvements and corrections have been made from each installation to the next until a very satisfactory type of installation has been developed.

An account of some of the salient features of several installations are abstracted freely from Mr. Russell's report to the Gas Association.

The Gloucester (Mass.) Gas Light Company installed five courses of Carborundum Bernitz blocks, 14 inches long by 8 inches high, each containing six holes in an 8-foot Gas Machinery set. In order to prevent injury from expansion, a cored block was made to a careful design so that any expansion would be taken up by the arch construction of the block. No trouble was encountered with this (or any other) Carborundum Bernitz block installation. There was no tendency whatever for clinker adherence and no deterioration from spalling or wear. This set of blocks ran from June, 1923, to December, 1924, making gas for about 2600 hours. Most of the blocks were in first class condition. The clay lining above the Bernitz blocks was badly broken up by the adherence of clinker there and some Bernitz block had been broken in the process. To overcome this, two rows of blank Bernitz blocks (having no holes) were installed in October, 1923, and this alteration completely stopped clinker troubles. During this period door jambs and arches of clay wore out rapidly, but were subsequently replaced with Bernitz designed blocks and troubles around door jambs and arches ceased. Many of the blocks were usable even after shutting down the machine. Fuel consumption was decreased, output per square foot was increased 20%, clinkering time cut in half and labor greatly reduced.

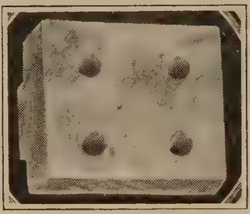

FIG. 2a.

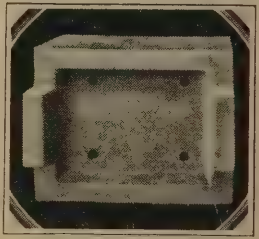

FIG. 2b.

At the Spencer (Mass.) Gas Company a new 5-foot set was equipped with five courses of Bernitz Carborundum blocks and two courses of blank Carborundum blocks. During the first 15 months' operation the clay blocks above the Carborundum were replaced twice. Later, the Carborundum lining was carried to the crown. Capacity of the machine is 20% greater than is expected from this type. There has been no clinker trouble in 15 months' operation.

Typical of the improved later installations is the one at Arlington, Mass., which was made in March, 1924, incorporating all the modifications brought out in the two years' previous experience. This set has now been in operation over 8000 gas-making hours. In this type installation, flues are formed between the inside and outside linings. When the air is blown into the ash pit, a large proportion of it, instead of going through the grates, passes up through the flues behind the Carbofrax lining and enters the fire through the holes in the block. This gives a perfect distribution of the air to the fire and overcomes the difficulty of clinker formation at the grate. During the run, steam passes through these holes giving a very thorough distribution with more regular and improved gas-making results. On the down run the blue gas passes out through these blocks. Due to the distribution of the air the combustion is less intense in any one location and the tendency is to form soft or unfused clinkers. The relatively cool air coming through the ports and blocks chills the clinker and prevents it from adhering to the side walls. The steam also tends to break and soften the clinker and causes it to shrink away from the lining. Figure 3 shows the Carborundum Bernitz lining at Arlington, Mass., after it had operated 4800 gas-making hours. Figure 1 is a close up view of the same lining showing the various kinds of bocks used. Figure 2 is a typical detail drawing of the Bernitz lining for a 9 foot set.

In one of the early trials silica blocks were used just above the top of Bernitz blocks. It was found that the heat and overcharging of the generator causes considerable clinker to form above the Carbofrax lining. In later installations this trouble was eliminated by the use of two or more air-cooled blocks without port openings. One of the many advantages of keeping the walls free from clinkers is the possibility of getting a longer run, thus increasing the yield and the efficiency of the set. For example, in one generator on a test run, over 24-hour periods, the output of the set increased 50%. There was also a great saving in labor and a reduction of fuel from 3 to 10% and of oil from 2 to 5%.

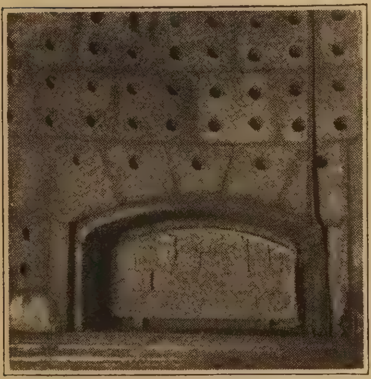

FIG. 3.

Accurate data has been kept on the costs of the lining at Arlington, Mass. This lining has now out-run eight clay linings. Inasmuch as it costs about $50 to shut down and start the set, appreciable saving has been made in this one item alone. In addition there is a labor saving in the "barring down" amounting to $750 in the life of linings. A comparison of the cost of Carborundum Ber[illegible] [illegible]mpared with clay is as follows:

Cost of Carborundum Bernitz lining		[illegible]
7 repairs to ordinary clay lining		[illegible]
Increase in first cost of Bernitz lining		$ 225
Saving in clinker, labor 30 minutes per day, 6 men, 400 days = 1200 hrs.	$750	
Saving in shutdown	300	1050
Total saving in favor of Bernitz lining		$ 825

Some other illustrative causes of the marked economies which have been actually secured by the use of the silicon-carbide Bernitz blocks, not only in lining costs but actual fuel saving, may be of interest.

At Glassboro, New Jersey, a Gas Machinery Company Generator 8 ft. 6 in. outside diameter was lined with silicon-carbide blocks of the Bernitz type. The average amount of fuel required per 1000 cu. ft. of gas was reduced from 27½ lbs. to 25 lbs. The amount of air required was materially reduced, and the air pressure required for successful operation was dropped about 20%. This plant has since installed a second lining in its other 8 ft. 6 in. generator.

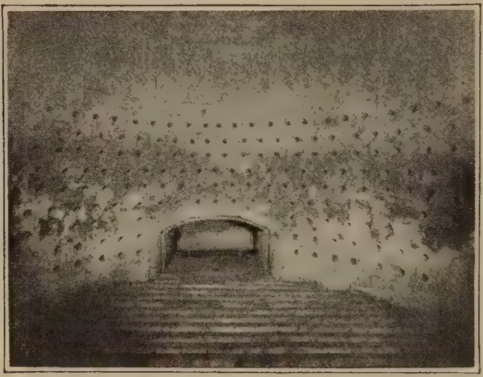

FIG. 4.

In another installation (at Paulsboro, N. J.) in a 5-foot generator, fuel has been reduced from 40 to 28 lbs. per 1000 cu. ft. of gas and the overall capacity has been increased about 30%. After 1600 operating hours the generator lining at this plant was in apparently as good condition as when originally installed. The shutdown was required because of the failure of the carburetor checkering. This plant has since installed its second lining in a 4 ft. 6 in. generator.

Practically identical economies were secured at another plant (Cumberland Gas Co., Millville, N. J.) in a 6-foot Gas Machinery Co. Generator. Gas was actually produced at a net saving of 30% over the best previous records.

The Wilmington Gas Company is now operating an eleven foot U.G.I. generator lined with Bernitz Carbofrax blocks. This generator has been in operation for 3000 hours and shows no trace of wear. The best previous record with clay linings was 900 hours. It has been possible to operate the generator for 24-hour periods with a single cleaning. The lon [illegible] required to clean the generator has been [illegible] ons, differences in fuel, etc., saving in clinker- [illegible] interest in certain cases. However, the cost of the lining [illegible] d several times over in the economies in consumption of materials. Not only has a saving in generator fuel been shown, but also in boiler fuel and in oil in many cases. The saving in oil is due to the fact that a better grade of blue gas is made, and requires less oil gas addition. The saving in boiler fuel is due to the fact that a lower pressure is required in Bernitz constructions than when all the gases are put through the grate. There are installations in which the fuel saving is greater than the saving in labor.

An important advantage which may be overlooked is a very large increase in capacity which has been universal when gas generators have changed to the Bernitz construction. While the first cost in comparison with a clay lining is always high, there has been no report that the saving did not justify the original expenditure and all who have used this have been enthusiastic about it.

A total of thirty-one Bernitz type units are now in operation. Twenty of these were installed in the year 1925. This type of lining for water-gas generators has passed the experimental stage and is a proven success.

The Carborundum Co.
Niagara Falls, N. Y.

THE HARPER ELECTRIC KILN[1]

By Francis A. J. FitzGerald

ABSTRACT

A description of the development of an electric kiln for porcelain and of the construction of an experimental commercial unit for firing biscuit ware at the works of the Buffalo Pottery Co. The kiln is of the continuous tunnel type and in the course of its development has been used for firing porcelain at temperatures as high as 1500°C (2750°F).

Several years ago the late John L. Harper, Chief Engineer of the Niagara Falls Power Company, conceived the idea of making an electric kiln for the heat treatment of porcelain. Originally he proposed to build this kiln in the form of two tunnels of considerable length heated in the center part by means of electrical resistors. The cars were to pass through the tunnels in opposite directions, in order that the heat generated by the kiln would be used to the greatest advantage. Harper knew that the periodic kiln, usually employed for the firing of porcelain, was thermally very inefficient, so that, in spite of the relatively high cost per unit of heat generated electrically, it would be possible to compete with fuel, because the electric furnace permitted of a more efficient design, particularly if the twin tunnel were used.

He also saw that in the electric furnace he could obtain a more perfect control of temperature and atmosphere and could thus make a better porcelain with lower kiln losses.

After making various experiments on electric furnaces Harper asked FitzGerald to coöperate with him in the development of the electric kiln and preliminary experiments were begun in 1909. These though carried out on a small scale were so satisfactory that they led to the preparation of plans for the building of a larger furnace. In 1923, arrangements were made with the Champion Porcelain Company of Detroit for experiments on a fairly large scale with the Harper kiln at the FitzGerald Laboratories.

Except in special processes, where high temperatures are with difficulty obtained with fuel, the cost of heating by electric current is bound to be much higher than with fuel. The cost per heat unit is, in general, much higher when generated by the electric current than by fuel; but where high temperatures are required it is sometimes possible to use the electrically generated heat with so much greater economy that, though the cost per heat unit is much higher, the total number of heat units used is so much less that the heating cost is less.

Another important consideration in comparing electric with fuel heat is that the use of the former permits of other economies which more than offset the higher cost of the unit of electric heat.

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[1] Received September 1, 1926.

In the early days of the electric furnace for steel making it was freely predicted that electricity could never be used for steel making except in the manufacture of crucible steel, because the cost of heating electrically would be so enormously greater than the cost of heating by fuel. This prediction has not been fulfilled because of the other offsetting advantages.

An analogous condition may be found in the pottery industry, because the ordinary periodic kiln, like the crucible furnace for steel, is thermally a very inefficient apparatus. It is quite possible, indeed highly probable, that with sufficiently cheap electric power the cost of the heat units in the electrically heated kiln might not be more; but where electric power is not cheap or where the electric tunnel kiln has to compete with an efficient fuel-fired tunnel kiln, it seems probable that the cost of the heat energy generated electrically would be higher than that obtained from fuel. As it is in crucible steel melting there seem to be other advantages in the electric kiln which would more than offset the higher cost of heat obtained electrically.

Experimental Kiln

It was a consideration of this kind which led to the abandonment for the time being of Mr. Harper's original plan of using the two-tunnel kiln with cars traveling in opposite directions. It was felt that the greater difficulties of construction in the two-tunnel kiln would offset the thermal economies which might be reached by it. Accordingly the experimental kiln consisted of a single tunnel 40 feet long. Figure 1 shows the central part of the kiln, including the electrically heated hot zone. Experimental work with this kiln was carried on for over a year and after this a larger kiln was constructed at the works of the Buffalo Pottery Company, Buffalo, N. Y. (Fig. 2.)

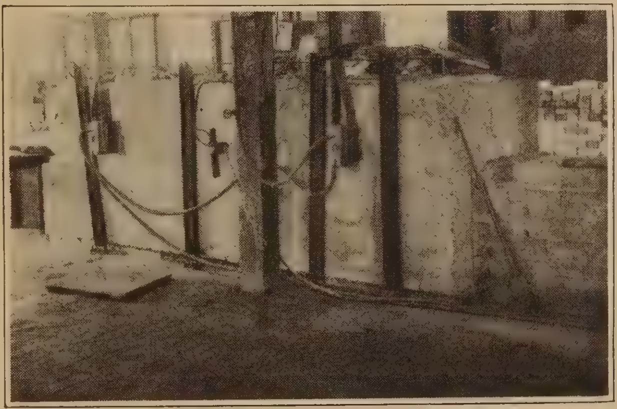

FIG. 1.

Kiln at Buffalo Pottery

The Kiln The drawing on Fig. 3 shows a plan, elevation, and two cross-sections of a semicommercial kiln designed for firing biscuit ware in the Buffalo Pottery Company's plant in Buffalo, N. Y. The kiln has a single tunnel 68 feet long with air locks 3 feet

5 inches long at each end. Nearly at the center of the tunnel is situated what is known as the hot zone, a transverse cross-section of which is shown. This zone is approximately 19 feet long. The entrance end of the tunnel, known as the preheating chamber, is about 24 feet long, the exit end, where the cars and their contents cool after leaving the hot zone, is approximately 25 feet long. Parallel to the kiln is a return track for the cars. At each end of the kiln is a transfer truck, running on tracks, which carries a single car from the return track to the entrance air lock or from the exit air lock to the return track. The tracks in the kiln are made of pipes through which water is circulated for cooling. The train of cars is pushed through the kiln by means of a ram driven by an electric motor through reduction gearing.

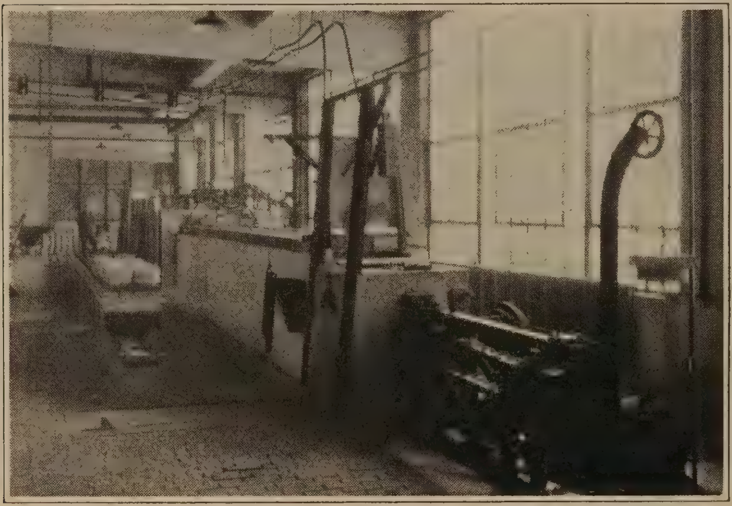

FIG. 2.

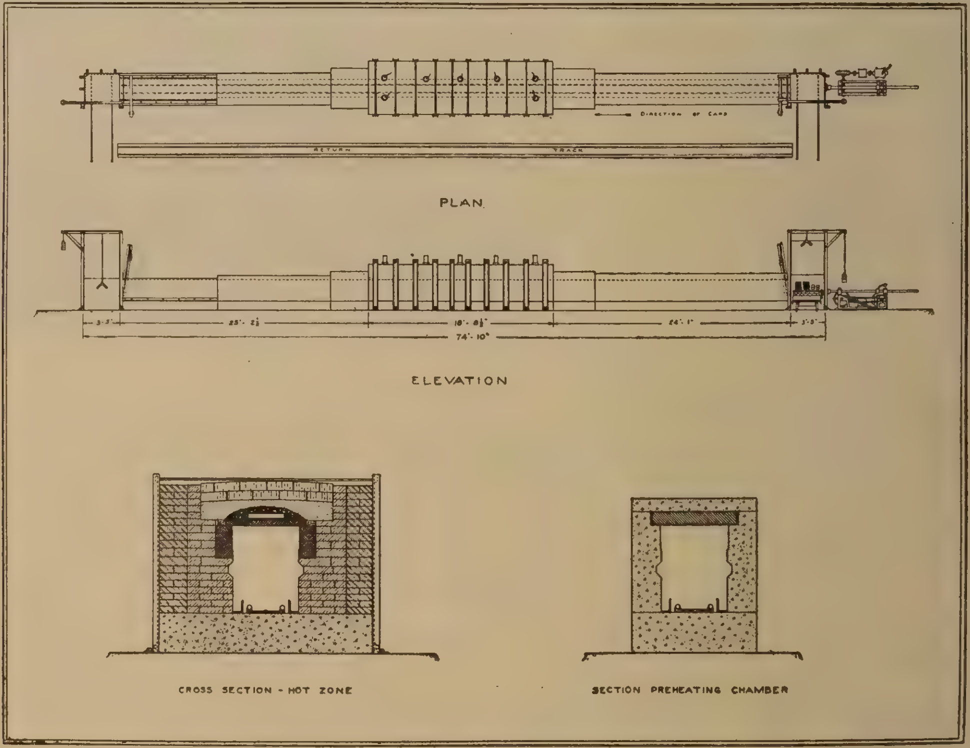

FIG. 3.

Metallic Resistors in Preheating Zone The preheating chamber carries on the side walls and roof metallic resistors, not shown in the drawing of this section in Fig. 3. Figure 4 is a photograph showing the disposal of the metallic resistor on one of the side walls of the preheating chamber. With these resistors the temperature of the ware on the cars can be raised to 900°C before a car enters the hot zone.

Graphite Resistors in Hot Zone The resistor in the hot zone is built up of grids made by cutting blind slots in alternate sides of Acheson graphite electrodes 1½ x 11 x 48 inches. The resistor is enclosed in the resistor chamber above the tunnel, as shown in the cross-section of the hot zone, separated from the tunnel by a refractory septum which forms the floor of the resistor chamber and the roof of the tunnel's hot zone. The resistor is made of four of these grids connected in series. The resistor chamber is constructed of a silicon-carbide refractory and is supported on silicon-carbide bricks which form the side walls of the tunnel in the hot zone.

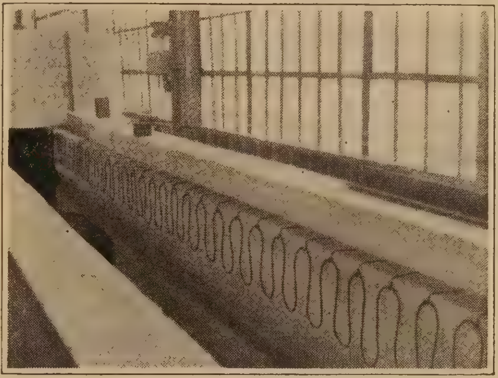

FIG. 4.

The electric current is brought to the resistor by means of a pair of graphite terminals at each end of the resistor chamber, passing through its roof, as shown in the plan, Fig. 3. The three intermediate terminals shown in the plan make contact with the connectors between the four graphite grids composing the resistor.

Insulation of Preheating and Hot Zone Care is taken in the construction of the kiln to provide the best possible heat insulation for the preheating chamber and the hot zone; but that part of the tunnel which forms the exit from the hot zone is not heat insulated any more than is necessary to prevent too rapid cooling of the ware.

Transformers The electrical equipment to supply current to the resistors consists of two transformer units, one used for the preheating metallic resistor, the other for the hot zone resistor. The preheating transformer unit has a capacity of 30 kilowatts and its secondary winding has taps which permit of varying the voltage at the terminals of the metallic resistor in the preheating chamber. There are two reasons for providing means for varying this voltage: first, because this particular furnace was designed for experimental purposes and it was not known before it was put into use just how much of the total power of the heating circuit should be used in the preheating chamber in order to get the best results; second, it was necessary to provide means for regulating secondary voltage of the transformer in case there were changes in the voltage of the power line connected to the primary of the transformer.

The transformer supplying current to the hot zone resistor has a capacity of 60 kilovolt amperes and by means of an induction regulator the voltage of the secondary circuit, going to the hot zone resistors, may be varied between wide limits.

Since it is necessary to maintain within narrow limits the power in the hot zone a regulator is provided which automatically operates a motor connected to the induction regulator, causing that apparatus to increase or decrease the voltage of the current supplied to the transformer so as to maintain the power in the resistor at whatever wattage is desired. This regulator actually maintains the wattage within plus or minus 0.5 kilowatt of the power for which it is set.

The Cars Figure 5 is from a photograph showing the construction of the cars on which the ware is carried through the kiln. The framework of the car is of cast iron, the wheel shafts running in Acheson graphite bearings so that they are self-lubricating. The iron aprons on the sides of the framework run in the sand seal, indicated in the two sectional views of Fig. 3. A hopper used to feed sand into the sand seal is seen in the side wall of the kiln just to the left of the airlock door in Fig. 2. The first layer of bricks laid on the car frame are heat insulators made of Sil-O-Cel. Above these is a course of fireclay splits arranged so as to form a radiation baffle running in the horizontal slots of the kiln side walls, as shown in the sectional views of Fig. 3. The next course is made of a special heat insulating brick made by the Carborundum Company and known as insulfrax bricks. These have excellent insulating properties and at the same time are highly refractory being quite unaffected for temperatures at least as high as 1300°C. Finally, on top of the car is a molded slab of silicon carbide, a refractory that is at the same time a relatively good conductor of heat. It will be observed that the Sil-O-Cel and insulfrax bricks are bevelled so as to form a radiation baffle, interlocking with the next car.

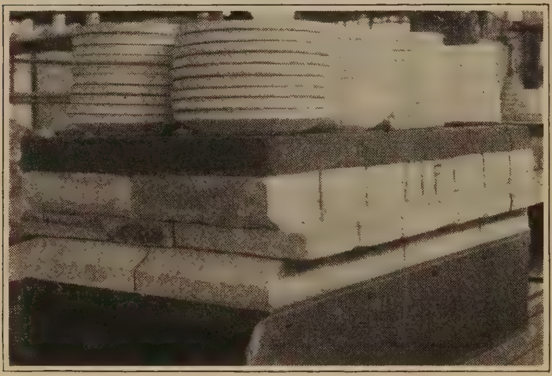

FIG. 5.

In Fig. 5 the car is shown loaded with setter plates, and when biscuit ware is firing it is loaded on the car in a similar way, no saggers being used. The object of making the top slab of the car of good heat-conducting material is to equalize the temperature over the bottom of the bungs as much as possible.

Heat Distribution in Kiln

In describing the hot zone of the kiln it was mentioned that the side walls supporting the recrystallized silicon-carbide septum plate in the hot zone (see cross-section in Fig. 3) were also made of recrystallized silicon carbide. This is done because this is an extremely good heat conductor. It might reasonably be supposed that the septum plate immediately below the resistor would be at a very much higher temperature than any other part of the inside of the tunnel radiating heat to the ware on the cars. While this part of the septum plate no doubt has a higher temperature than the rest this excess is actually small because of the high heat conductivity of the recrystallized silicon-carbide septum and bricks.

In firing biscuit ware properly in any kind of kiln there are two factors which must be considered, time and temperature, for there is a limit to the rate at which it can be heated, and the temperature to which it must be raised lies between certain limits.

In heating ware in a tunnel kiln these same two factors, time and temperature, must be considered. Assuming that the kiln walls are maintained at a fixed temperature the rate at which the ware is heated will depend upon the rate at which it travels through the kiln and consequently its temperature at any point in the tunnel will depend upon the uniform rate at which the cars are moving and upon the temperature gradient in the kiln.

Data on Design

The data for the design of the experimental kiln were as follows:

Dimensions of car top	18 x 34 inches
Maximum height of ware	6 "
Car top to septum	8 "
Car load:	
3 bungs 7 inch plates	52.5 pounds
3 bungs 4½ inch plates	28.5 "
1 bung 5½ inch plates	8.5 "
Miscellaneous	9.0 "
Total weight of ware	98.5 "
Output per hour	1 car

To complete the data required for the design of the kiln it would be necessary to have a curve with abscissas as distances from the entrance to the tunnel and ordinates as temperatures of the ware. As the data for this were not available it was necessary in preparing the design to assume a curve of this kind.

The metallic resistors for the preheating chamber and the graphite resistors for the hot zone were designed to give the required power distribution in the tunnel. Since this was based on an assumed car position-temperature curve it was quite certain not to be correct, therefore some method of adjusting it was required. Accordingly the terminals of the grids making up the hot zone resistor were used for connecting external shunts for varying the power in each grid. This is satisfactory for experimental work; but for commercial practice the more economical method of varying the power by changing the voltage at the terminals of the grids would be employed.

This paper being intended merely as a description of the construction of the electric kiln, a description of its operation will be given at a later date.

My thanks are due to the Buffalo Pottery Company for permission to publish the photographs and some of the data in this paper.

The FitzGerald Laboratories
Niagara Falls, N. Y.

SOME FUNDAMENTALS OF TERRA COTTA[1]

By Harry Spurrier

ABSTRACT

Terra cotta is not a definite material. Considerable difference of opinion exists as to suitable structure and composition. There are more differences between different makes of terra cotta than there are in opinion as to what it should be. Microscope study of thin sections of terra cotta is a valuable method of examination. The voids in terra cotta are of more than one kind and origin. The grog used in terra cotta is frequently unsuitable as to character and size. A fuller knowledge of fundamentals will probably much alter ideas as to suitable grog. A test for internal stress is described. Terra cotta was tested for osmotic action. The internal degradation of terra cotta is demonstrated by two different methods. A number of slides are presented being typical of certain characteristics.

During the past two or three years the writer has been called upon to make tests on terra cotta, having in view some specific objective. It therefore became necessary to investigate the literature and become acquainted with the customary tests and the deductions drawn from the results of these tests. Furthermore a personal need was felt for an intimate knowledge of the structure of terra cotta, both macroscopic and microscopic. As these preliminary investigations progressed it was borne home very strongly that terra cotta was not a definite material, either as to composition or structure. An investigation of these differences was made, to develop if possible, a connection between the mental concepts of terra cotta makers in regard to an ideal terra cotta. This effort tended to add to the confusion in regard to what terra cotta should be.

Experiments were then made purely for personal guidance in regard to physical characteristics of the varieties as found upon the market. Again there was recorded an enormous divergence between different varieties and also between different specimens of the same manufacture.

This difference between different samples of the same manufacture can and does arise from a number of contributory factors, which may be classed in the following general way: (1) differences of which the maker is ignorant; (2) differences of which the maker is cognizant, but to which he is indifferent; (3) differences arising from variations in raw material (*a*) unavoidable, (*b*) avoidable, but tolerated; (4) differences arising from lack of proper control of materials and machinery; (5) differences arising from variations in the chemical and physical character of the ingredients brought about by conditions of supply, etc.

Aside from all this there remains the fact that there is no agreement as to what constitutes the best terra cotta.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Terra Cotta Division.)

It would, I believe, be impossible to get two manufacturers of terra cotta to write out independent specifications for the material, which would show particular agreement. This probably arises from the fact that there are a number of variables to contend with in each individual case, as much as from difference of individual ideas.

There are, however, a number of points about which a well-defined general agreement could be established, which at present lack any great degree of definition.

Microscope Survey

A microscopic study of a considerable number of bodies brought out several points of fundamental importance, attention to which might improve the body.

Voids There was at once noted a very wide difference in the amount of voids in any given area, varying all the way from well over 40% down to how little I do not know, but never very little. The voids here considered are not those of large air inclusions consequent upon the body not being rammed home, but those easily distinguished as being consequent upon the mixing operations.

At first these voids could not be related to any particular direction or orientation and they seemed to lack any character that would aid in diagnosing a cause for their distribution. As experience accumulated it was observed that their occurrence was commonly associated with coarse grog particles and it was discovered that the movement of such coarse particles in working the body caused a separation of the body and consequently a trailing void. It should not be difficult to remedy this state of affairs, especially in aggravated cases.

Grog The heterogeneity of the grog in many cases is cause for a great number of defects, which, taken collectively, are serious enough to call for careful attention.

The practice of using grog without regard to its physical character is not to be recommended as it is the cause of considerable disturbance. The question of coefficiency of volume under temperature changes has received all too little attention. In numerous cases the grog particles had fluxed to the body, only to be ruptured as the body of higher cooling shrinkage pulled them apart; and, at times, exactly the reverse of this phenomenon had taken place.

Such a condition presents an admirable nucleus for cooling cracks to start and when once started no one can foresee the end. This merits serious consideration with excellent prospects of an abundant return.

If grog is made from the same clay as the body and fired to the same time and temperature schedule, it would be possible to revise much of the accepted data as to the function of grog and also the desirable limits as to size and quantity. It is confidently believed that grog data has been amassed with so many variables as to make some of the conclusions of questionable value.

Study of Sections It is quite certain that coarse grogs make for excessive porosity, which will later be shown to be undesirable. Much valuable information accrued during the cutting and grinding and mounting of the specimens used in this work, and although such evidences as those referred to later require some experience and a little skill for their proper interpretation, the results are well worth the work involved.

The pieces of terra cotta used were never hammered or broken, but the portion used for the slide was invariably sawed out of the solid piece, with a revolving disk of thin sheet metal, provided with a large number of fine indents made by gently striking the disk with a knife blade. The disk was armed with a mixture of 120-mesh Carborundum and oil.

A little experience with the sound made during this cutting soon enables one to tell accurately the nature of the body being sawed, but it is impossible to describe this in words.

It will also be noted that soft, friable, highly porous, and hard bodies, all give their characteristic note and sensation to the hand during sawing. The soft and porous bodies take longer to cut than the dense and hard bodies and are far more difficult to handle. For instance, glass cuts more easily and faster than terra cotta.

Having cut the desired section, it is ground down to a plane and very smooth surface on one side. The specimen is now washed free from oil and Carborundum and dried thoroughly; it is then cemented to a section of plate glass which has been ground on one side and very carefully measured with a micrometer.

The further grinding of the specimen is continued with the necessary precautions until the mount measures one or two thousandths of an inch greater than the plate glass.

The fine grinding being finished, the thin section is removed from the glass plate by the aid of hot turpentine and a section lifter, using the precautions always necessary in preparing petrographic sections.

The delicate section is now washed in ether and dried.

We now arrive at the important point that has rendered the foregoing description necessary.

We have secured a plane slice of terra cotta somewhere between one and two thousandths of an inch in thickness, and with such a degree of attenuation the specimen is quite flexible. Should there have been any internal strain in the body it will now cause the thin section to curl up a little, and this is really a very delicate means of demonstrating the presence of internal strain in a body. Even if no microscope study is to be undertaken this simple procedure is well worth while to anyone desirous of knowing somewhat of the strains in terra cotta.

There is quite a difference of opinion as to whether a close or open body is the more desirable, and while allowing perfect freedom to all to settle this moot question in their own way, the results of some carefully made experiments might present some new angles to both the tight and loose arguments.

The flexibility of even a moderately thin piece of terra cotta about .005 inch thick is very small indeed and if porosity aids flexibility, such aid is amply supplied by a degree of porosity far less than that exhibited by the densest piece of terra cotta I have ever seen. I hope in the near future to have precise figures on this.

Osmosis as Cause of Terra Cotta Breakdown

It had occurred to me that possibly osmosis might be a factor in the breakdown of terra cotta. The speculation looked fairly plausible, when considered in the light of the fact that terra cotta shows a solubility as high as .75 of 1%. Suppose we have a free standing piece of terra cotta well saturated with water, or even only locally saturated; the water of saturation becomes a weak solution of the soluble portion of the body. If the sun should shine upon a rounded surface, or for any cause some of the solution should be evaporated locally, say on a curved exterior, the solution would become locally more concentrated and then according to the laws of osmosis a flow will develop directed toward the area of concentrated solution and from the inner areas of less concentrated solution, thus setting up osmotic pressure. Should this flow develop a rate greater than that of the natural passage of the liquid through the body, it is clearly conceivable that rupture might ensue because osmosis can and does develop very high pressures indeed.

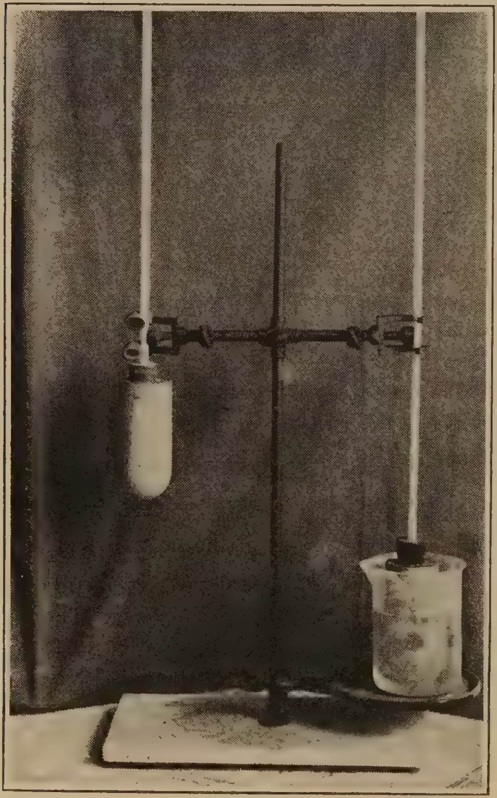

FIG. 1.

Accordingly I had some tubes of terra cotta made similar to a very large and thick test tube. The opening was ground to a true circle and the upper one inch was well soaked with melted paraffin wax; a good rubber stopper fitted with a straight and vertical glass tube completed the special part of the apparatus.

The terra cotta tube and part of the glass tube were filled with a molar solution of salt and the terra cotta tube was immersed in a beaker of distilled water. (See Fig. 1.)

Internal Structure Fractured by Freezing and Thawing

Under these conditions had there been any osmotic action, the distilled water would have forced its way into the tube and developed a pressure which would have been indicated by a rise of the salt solution in the glass tube. However, no such result occurred and it became evident that osmosis may be disregarded as a factor in the breakdown of terra cotta insofar as large areas are considered. Further reflection led me to believe that there might be and probably was a considerable change in the internal structure of bodies, occasioned by repeated freezing and thawing of wet terra cotta, long before the spalling of the exterior of the body takes place.

Accordingly a set-up was used similar to that described for the osmosis test, but with this difference: the tube was filled nearly to the top of the glass with distilled water and the rate of the descent of the water level in the glass tube was taken as a measure of the passage of water through the body, say so many millimeters in 20 seconds; having established this rate with a stop-watch, the terra cotta tube was placed in a water tight can and immersed in distilled water and the whole frozen solid and chilled to a temperature of −10°C.

After thawing, the experiment previously described was repeated with the interesting result that the rate of water flow through the body had increased more than threefold, by simply freezing the body once.

On each successive freezing and thawing an increased water flow rate was recorded.

This can be interpreted in only one way, namely, the passage ways by which the water passed through the body had been increased by internal disintegration of the body.

It was sought to confirm this interesting finding by attacking the problem from a rather different angle. If the terra cotta suffers internal disintegration in freezing, it was extremely likely that some, at least, of the closed pores would be broken open and that, were it possible to make per cent porosity tests with sufficient accuracy and constancy, this would be a crucial test.

During many porosity determinations a method and technique have been developed which have proved very accurate indeed and although a porosity difference of very small magnitude was anticipated, it was confidently believed that it might be very positively measured.

Accordingly, two 10-cm. cubes were prepared and the porosity determined with the utmost care, even to the weighing of the bodies in a completely dried state, which made a difference of .5 gram on a weight of over 800 grams and atmospheric humidity of 32.5% at a dry bulb temperature of 64°F. In each case the porosity was found to be about 1.25% greater after freezing than before.

It may therefore be stated that the terra cotta body suffers internal breakdown at the very first freeze while in a saturated condition, that this degradation is cumulative, and the spalling on the exterior is probably only the full stop at the end of a long chapter, in the earlier stages of which a great deal takes place that to date has escaped our attention.

Another factor not commonly recognized might be well worth mentioning in closing. Suppose that a free standing piece of terra cotta becomes thoroughly wetted internally and is then frozen at a temperature of about 28°F. A surface of frozen material is produced and as the frost goes deeper the enclosed water expands in the process of freezing; exudation is arrested by the ice coat already formed and considerable pressure must be developed internally. If now the temperature drops rapidly to about zero, the internal ice will suffer a considerable contraction and drag vigorously on the small particles to which it is attached. We now have a very destructive agent at work and, withal, a very subtle one. This contribution is offered in the hope of stimulating research in this and other directions with the aim that some day we may be able to state precisely what terra cotta should be, both compositionally and structurally.

Northwestern Terra Cotta Co.
Chicago, Illinois

PERSONAL EXPERIENCES AND NATIONAL LIFE AS SUBJECT MATTER FOR DESIGN[1]

BY MYRTLE MERRITT FRENCH

ABSTRACT

Artists who lack ideas for design often resort to copying something made by a different people to express the life of a different age. As a result the design does not express America and is not in harmony with the natural expression of the American home. Many interesting symbolic designs have been worked out in class using personal experiences for the subject matter. Thus the designs have a new interest both to the artist and the public. If American industrial art would encourage the artistic use of the wealth of material in our national life, the products produced would be given a soul which would make them alive.

For some time much energy has been spent on scientific and technical subject research; it is high time that a few now turn the attention to art research to discover how the artistic quality of ceramic wares may become a living expression of vitality and to find out how that force can best fit into a bigger and finer educational and commercial scheme.

The idea of using personal experiences and national life as subject matter for ceramic design grew from the feeling of a need of something vital to express in order to give individuality and strength to patterns. It was observed that when the students did pageantry for their big annual ball, there was no lack of real beauty through their patterns and, yet, when it came to decorating a piece of pottery, too often they were baffled or resorted to the same old ideas of a peacock, windmill, Japanese lantern, or boat. Far too few developed an original expression on any subject.

When a student was asked why the class did such fine decorative things in pageantry but had so few ideas in pattern for a pot, the reply was, "Oh! the pageant is our own expression for our own lives. It means something to us, we are free to do as we choose."

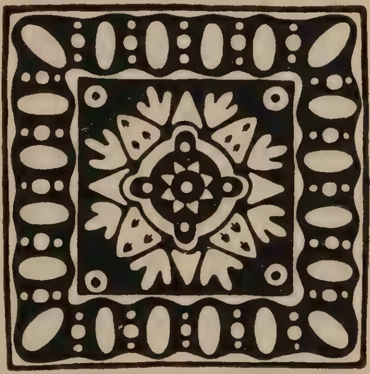

FIG. 1.—Sketch from an incised tile made by a student of the Art Institute of Chicago. It symbolizes an auto trip. Explanation: In the center is a tourist camp with a fire around which are eight tourist tents. Outside that is the road (in white) with gas stations at intervals. Farther out are symbols of mountains and foothills, some of which are wooded. Between them is the sun. In each corner of the square center is a spot representing "the places we didn't get to see." The border symbolizes watermelon and other fruit eaten along the way.

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[1] Presented at the Annual Meeting, AMERICAN CERAMIC SOCIETY, Atlanta, Ga., Feb., 1926. (Art Division.) Received September 23, 1926.

That remark was worth considering. The result was the following experiment.

A tile problem was given, the design of which was to represent some personal experience treated symbolically. The tile was to have a beautiful pattern for both observer and creator, but to the latter it must have a significance which might or might not be apparent to the former. The pattern *must not* be a picture, but a symbol. Already the students had known of the Indian symbolism and were urged to catch that spirit in expressing their own lives by their *own* symbols. The architectural plan of each pattern was first chosen and then the fun began. A few knew exactly what they wanted to say, but most of them floundered for a time. By the end of the first lesson nearly every member had made a good start. When the tiles were completed they were the best set ever produced in any class by a similar group, and many said they had enjoyed making them more than any other design.

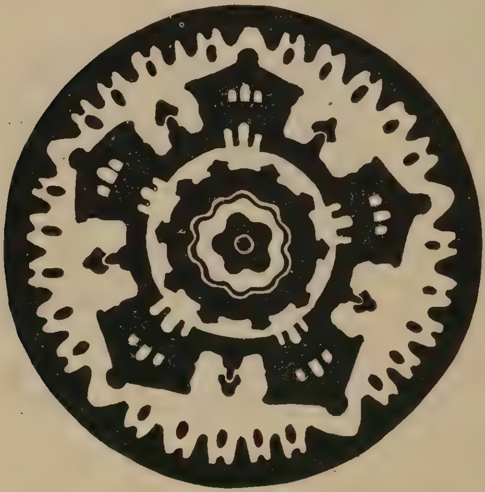

FIG. 2.—Sketch from a plate made by a student using colored glazes. An incised line separated the colors. It symbolizes the most important experiences in the life of the student. Explanation: The central flower-like form symbolizes the family of five as a center. Grouped next to it are the schools attended before going to the Art Institute of Chicago. The largest dark spots suggesting the shape of a building represent the Art Institute. Between them is a mountain in Colorado on top of which is a cabin. The larger points at the border represent the mountains, the smaller ones, foot-hills. The isolated black spots symbolize a special hill.

The following year a plate design in the same spirit was added to the tile problem, but the subject matter as suggested was to be a national institution instead of a personal experience. Quite a list was given, some of broad scope and some of narrower, with a chance to choose a different subject if desired. The following is an outline.

1. **Transportation** Symbolized by a movement in a particular direction: (*a*) aeroplane, (*b*) steamer, (*c*) electric, (*d*) horse, (*e*) auto, (*f*) rail, and (*g*) bicycle.

2. **Industries** Symbolized by a feeling of growth, probably upward: (*a*) mining, (*b*) agriculture, (*c*) manufacturing, (*d*) construction, and (*e*) municipal activities.

3. **Business** Symbolized by repetition: (*a*) merchant, (*b*) baker, (*c*) laundryman, and (*d*) restaurant.

4. Industrial Arts Symbolized by more delicacy: (*a*) printing, (*b*) weaving, (*c*) blacksmithing, (*d*) cabinet making, and (*e*) pottery.

5. Day Labor Symbolized by strength of the individual: (*a*) street cleaning, (*b*) street repairing, (*c*) ditch digging, and (*d*) teaming.

In working out this problem most of the students took material of much narrower scope than outlined, such as apple industry or the growth of plants in a conservatory. Only the more intellectual ones tackled the broader subjects. One attractive plate design represented immigration, the home land in the center, the voyage across the ocean to the new country at the border.

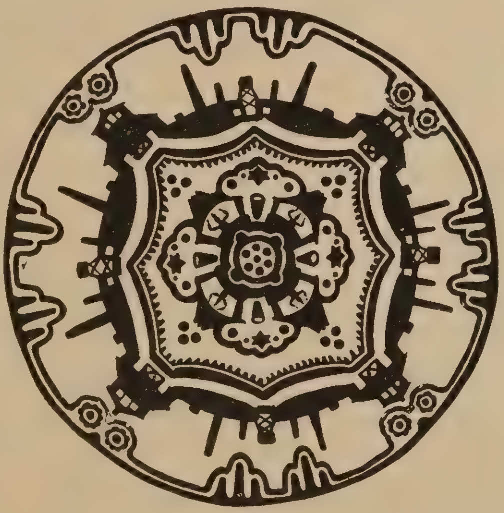

FIG. 3.—Sketch from a plate made by a student using blue slip on cream colored clay, and glazed with a colorless transparent glaze. It symbolizes a visit to Hull House Settlement in one of the foreign centers of Chicago. Explanation: In the middle is represented a crowded center. Around it are four street booths in which fat women are waving their arms to attract sales. Between the booths are fruit baskets, over the baskets the Jewish star, and on each side of the star are old ash cans. Over the roof of the booth is the sign of the three balls. Around the central medallion is a border of cheeses hanging in the shop windows along the street. The heaviest dark border toward the edge, represents Mrs. French's little bungalow home built on the roof of the Boy's Club at Hull House as main spots. From it can be seen the city as a mass, above which are chimneys and water tanks. The outside border symbolizes the sun half-hidden by the atmosphere and clouds of smoke hanging over the city.

Students in pottery never having had design have been given the idea of the personal experience with good results. Without art training a beginner is usually scared because he has nothing to say, but when he can tell his own story by means of symbols instead of pictures, often he is freed. Many people have a feeling for the architectural plan of a design, and usually that is all the beginner of design has. With the added possibilities of symbolizing something from personal experience, a good decoration often follows, otherwise a design suited to embroidery, advertizing, woodcarving, or metal would be copied and the result would be unsatisfactory.

In using this idea for teaching, the first difficulty the instructor has to face is the impulse of the student to picture the experience, because he knows pencil and paper but does not know clay. He will soon discover clay and get a feeling for his material, if the instructor insists upon a bold, direct handling of the clay. The second difficulty is, that the student gets so interested in the picture (or symbol, when he has caught the spirit) that he forgets the pattern. By making him criticize his own tile for pattern and work with it [illegible] side up or corner-wise, he gets an original, live pattern of his own [illegible] generally as good as, and usually better than, what [illegible] produce by a rehashing of the expressions of an unknown person with different ideals, no matter how beautiful that expression has been. He has said something and he has said it in his own way, a great triumph over a mechanical copy or a weak reiteration of what some one else said beautifully.

If the subject matter of the natural expression of a child is observed it will be noticed that it is his own experience in some form, his every day life, his imagination or stories or pictures, which have held his interest. Through a study of the best primitive art it is found that the patterns invariably symbolize something vital. The art of the Mexican schools, which developed such fine expression, was founded upon seven symbols of their lives. Some of the finest old Persian rugs are symbols of the plan and activities of the little village where the rug was made. And so we could continue indefinitely. American industrial art, as a whole, has become mechanical and devitalized. It is up to us as educators and producers to give our art expression, a soul which will make it live.

Art Institute of Chicago
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ORIGINAL PAPERS

A PRELIMINARY PETROGRAPHIC STUDY OF PORTLAND CEMENT[1]

BY JOSEPH L. GILLSON[2] AND ELMER C. WARREN[3]

ABSTRACT

A microscopic study was made of the clinker of five commercial brands of cement. Three crystalline compounds make up over 95% of these clinkers. The optical properties of two of these were determined; one, the principal constituent, is uniaxial and negative and has indices of 1.726 and 1.730. The other is biaxial and positive and has indices of 1.718, 1.720 and 1.733. This compound was found in both the clinker and the set concrete, proving that it is an inert substance without hydraulic properties. The optical properties of these compounds are not the same as those of any of the members of the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system determined by Rankin and Wright.

Several petrographic studies of Portland cement have been made by Colony,[4] by Rankin and Wright,[5] by Rankin,[6] and by Bates and Klein.[7] Colony worked with thin sections of Portland cement, while the other investigators worked with synthetic, pure compounds of calcium, aluminum, and silica. They determined the possible combinations of these elements under laboratory conditions and then suggested what the probable mineral constituents of Portland cement are. Naturally, the question suggests itself: are the actual constituents of Portland cement clinker identical in their properties with the synthetic materials which have been formed under laboratory conditions?

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[1] Received June 22, 1926.

[2] Assistant Professor of Mineralogy, Mass. Institute of Technology.

[3] Assistant, Dept of Physics, Mass. Institute of Technology.

[4] R. J. Colony, "Petrographic Study of Portland Cement," *School of Mines Quart.*, Vol. XXXVI, Nov., 1914.

[5] G. A. Rankin and F. E. Wright, "The Ternary System $CaO\text{-}Al_2O_3\text{-}SiO_2$," *Amer. Jour. Sci.*, 39 [4], 74–75 (1915).

[6] G. A. Rankin, "Portland Cement," *Jour. Frank. Inst.*, June, 1916, pp. 747–84.

[7] P. H. Bates and A. A. Klein, "Properties of the Calcium Silicates and Calcium Aluminates Occurring in Normal Portland Cement," U. S. Bur. Stand., *Tech. Paper*, No. 78, p. 28, 1917.

In order to answer this problem, the authors made a petrographic study of five[1] common brands of Portland cement. It was found that the ground clinker as sold in retail stores, is too fine to be readily studied by optical methods. Accordingly, samples of the unground clinker in the form in which it comes from the kiln were obtained from the manufacturers. This clinker was then ground only to 140-mesh, a screen which yields about the optimum particle size for working with grains mounted in index of refraction liquids under the petrographic microscope. Although the great majority of the crystals in the clinker are very small, the larger ones are preserved by this degree of grinding, and on them the interference figures so necessary to the optical determination of the crystals can be obtained.

Minerals in Clinker

Three minerals make over 95% of the mineral composition of each of the five clinkers. Although at least two other crystalline constituents occur in subordinate quantities, they can have little or no effect on the properties of the cement. They were not determined optically.

Of the three major constituents, two greatly predominate and large enough crystals of them occur to permit optical investigation. The third substance is present as a very finely divided brownish powder, which forms a coating on the grains of the other constituents.

The optical properties of the three major constituents are as follows:

1. Uniaxial, optically negative, with indices of refraction of 1.726 and 1.730. The mineral is very abundant and occurs in colorless crystals.
2. Biaxial, optically positive, optic angle about 20°, with $\nu > \rho$ extreme, and indices of refraction of 1.718, 1.720, and 1.733. It is less abundant than No. 1, and occurs as clusters of small, spherical grains having a brownish color and which are held in a matrix of the third constituent.
3. The brown powder which coats grains of the other constituents, particularly the second, has an index of refraction greater than 1.86, and resembles iron oxide. It may represent the mineral containing the iron known to be in Portland cement. The brown color of the powder seems to be a superficial stain, for in some cases clear crystals can be seen beneath the coating. The grains are always too minute to permit optical study.

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[1] Atlas, Lehigh, Edison, and two brands of Iron Clad.

By comparing these properties of the actual constituents of Portland cement with the properties of the artificial materials, it is clear that the commercial cement consists of minerals whose properties are not identical with those of the synthetic compounds. The following data are from Rankin and Wright.[1] They are the optical properties of the several compounds of calcium, aluminum, and silica that these men were able to make in the laboratory.

Composition	$\gamma \cdot 2CaO \cdot SiO_2$	$\beta \cdot 2CaO \cdot SiO_2$	$\alpha \cdot 2CaO \cdot SiO_2$	$\beta \cdot 12CaO \cdot SiO_2$	$3CaO \cdot SiO_2$	$3CaO \cdot Al_2O_3$
Crystal system	Monoclinic(?)	Orthorhombic or monoclinic	Monoclinic or triclinic		Monoclinic(?)	Isometric
Crystal habit	Prismatic	Irregular grains—prisms	Irregular grains	Equant grains	Equant grains	Equant grains
Cleavage	001 100	Poor			$p(111)$	$p(110)$
Elongation	r α					
Optical orientation	$b=\beta$ $c:\gamma=3°$(?)		$c:a=18°$		$c=\gamma$	
Index of refraction α	1.642	1.717	1.715			
“ β	1.645		1.720			
“ γ	1.654	1.735	1.737	1.715	1.715	1.710
Character	−	+	+	+	−	
Optic angle	$2E=52°$	Large	Large	Uniaxial or small angle	Uniaxial or small angle	

The only resemblance between the commercial product and the synthetic minerals lies in the similarity between $\beta 2CaO.SiO_2$ and the biaxial positive constituent found in the commercial cement. However, the optic angles of the two minerals are not the same, indicating that there is some difference between them. The most abundant constituent of the commercial cement does not have properties closely similar to any of the synthetic minerals, the index of refraction being higher than that of $3CaO.SiO_2$.

The two major crystals differ in specific gravity, and an attempt was made to utilize this fact in the preparation of fractions for analysis in the hope that the chemical composition of each would be determined. A complete and clean separation of each mineral could not be realized, due to the intimate intergrowth of the several constituents, but two fractions were obtained, one with about 60% of No. 1 and 35% of No. 2, and another with about 75% of No. 2, and 15% of No. 1.

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[1] G. A. Rankin and F. E. Wright, *op. cit.*, p. 3.

These two fractions were chemically analyzed by L. F. Hamilton of the chemistry department of the Massachusetts Institute of Technology. The analyses of the two fractions were so similar that no satisfactory conclusions of the compositions of the two major constituents could be drawn. In fact, the similar analyses suggest that the two major constituents of Portland cement are calcium aluminum silicates. However, the impure nature of the analyzed fractions permits little faith to be placed in the analyses.

Set Cement

It was not within the scope of this investigation to study the set cement, but a number of specimens were examined. The microscope shows crystals in the neat cement which differ from those in the dry clinker, but the brown clusters of spherical crystals of the biaxial positive mineral are found in the set cement as well as in the dry clinker. Evidently this constituent is inert and is unaffected by water, a fact further substantiated by X-ray examination.

The X-ray study of the clinker and of the neat cement was done by Hull's method, which consists in powdering an amount of the substance under investigation and then placing some of this powder in a beam of monochromatic X-radiation. The powdered crystals will diffract the beam according to Bragg's law. The results show that the same diffraction lines are produced by both dry clinker and neat cement. This indicates one of two things. Either no new crystals are formed on hydration, or one or more constituents are present in both clinker and set cement. No extensive study was made by this method, but since new crystals are known to form, the presence of the same diffraction lines in the spectra given by the clinker and the neat cement proves that there is at least one common constituent.

This article is a preliminary report, and it is planned to continue the study of cement by the petrographic microscope with the hope of proving just what these constituents are, and of finding out what are the new crystals that do form during setting.

The authors take this opportunity to express their thanks to C. L. Norton for arranging the financing of this investigation through the Division of Industrial Coöperation and Research of the Massachusetts Institute of Technology, and to J. T. Norton for his aid and interest in the X-ray analysis of the clinker and neat cement.

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THE THEORY OF PICKLING OF SHEET IRON AND STEEL FOR ENAMELING PURPOSES[1]

By Homer F. Staley[2]

ABSTRACT

The fundamental principal of efficient pickling is that efficient pickling does not depend on the solution of a large amount of metal but on the solution of a very thin layer of metal directly beneath the scale, rapidly and with copious evolution of hydrogen. The activity of an acid solution depends on the amount of acid present, the fraction of the acid that is ionized, and on the speed with which the ions move. Since the electrical conductivity of an acid solution is a measure of both the hydrogen-ion concentration and the speed at which the ions move, the electrical conductivities of a series of acid solutions indicate the relative activities of the various solutions. The most effective concentrations of acid lie between 15 and 20%. Heating acid solutions reduces their viscosity and renders the particles more mobile, thus increasing the activity of the solutions. Sulphuric acid is cheaper in first coat than hydrochloric acid, but the latter acts more rapidly and the pickling is completed with less solution of iron. Additions of small amounts of common salt (sodium chloride) have a marked effect on increasing the rate of pickling of sulphuric acid baths. This is due to the formation of a corresponding amount of hydrochloric acid. The chief action of addition agents is to reduce the amount of acid vapor in the fumes from pickling vats and thus permit the use of highly efficient concentrations of acid (between 15 and 20%). Hydrogen absorbed by metals during pickling may be largely removed by immersing the metal in boiling hot water for a few minutes.

Introduction

In enameling technology "pickling" consists of treating the metal to be enameled with acids. The object of pickling is to remove any oxide and slag scale adhering to the surface of the metal.

Mechanism of Pickling Contrary to earlier theories, recent investigations have shown that the actual solution of oxide of iron in the pickling operation is almost negligible and that the principal action is the attack of the acid on the underlying metal. The acids penetrate the coating of scale and attack the metal beneath. The metal is eaten away with evolution of large amounts of hydrogen and the scale is loosened from the surface of the metal. The iron goes into solution as ferrous sulphate or ferrous chloride, as the case may be. Some of the hydrogen formed is absorbed by the metal while the remainder passes up through the solution and into the air together with the steam and any other gases. The scale which is but slightly, if at all, attacked, falls to the bottom of the bath.

The fundamental principal of efficient pickling is that efficient pickling does not depend on the solution of a large amount of metal but on the solution of a very thin layer of metal directly beneath the scale, rapidly and with copious evolution of hydrogen.

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[1] Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Enamel Division) Received June 22, 1926.

[2] Manager, Ceramic Dept., Metal and Thermit Corp., New York City.

Factors that effect the efficiency of the pickling operation are:

1. Concentration of acid
2. Temperature
3. Kind of acid
4. Salts formed in the bath
5. Salts added to the bath
6. Addition agents
7. Use of electric current

Effect of Concentration of Acid

Numerous investigators have studied the effect of variation of concentration of acid in the pickling bath on the rate of pickling. Data and curves showing this effect have recently been published by J. T. Robson.[1] It has been found that whatever acid or mixture of acids is used, the effect is always the same. With very dilute acid solutions the time of pickling is long. As the concentration of acid increases the time of pickling rapidly decreases and reaches a minimum at between 15 and 20% actual acid. As the concentration increases beyond that point, pickling gradually slows up, and when very high acid concentrations are reached, pickling becomes very slow or stops entirely.

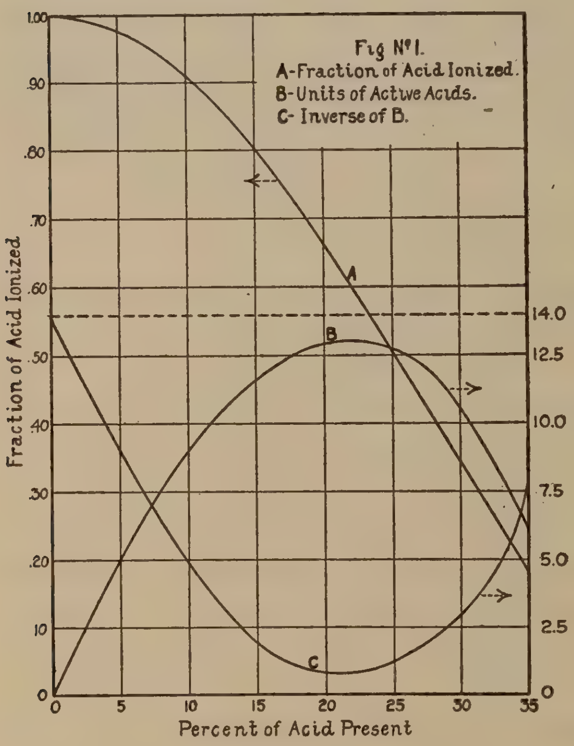

FIG. 1.

The explanation of this seemingly curious variation in time required for pickling with variation in concentration lies in the fact that when acids are present in solution, only a certain percentage of the acid is active. This part is said to be ionized, because the acid molecules are split up into hydrogen ions and non-metallic radical ions. These hydrogen ions are the part of the acids that give them their characteristic properties and are the part that really do the pickling. Another factor is the speed with which the ions move. Therefore, the activity of an acid solution depends on the amount of acid present, the fraction of the acid that is ionized; in other words, on the hydrogen-ion concentration, and on the speed with which the ions move.

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[1] *The Enamelist*, July, 1925, pp. 15–19; Oct., 1925, pp. 14–17; Nov., 1925, pp. 5–8.

Effect of Concentration on Hydrogen-Ion Concentration

It has been found that the fraction of acid that is ionized or active is very high in dilute acid solutions and that this fraction decreases at an ever increasing rate as the concentration of acid in solution increases. A typical example is given in Fig. 1, curve *A*. The units of active acid shown in curve *B* are found, of course, by multiplying the percentage of acid present by the fraction that is ionized; in other words, curve *B* shows the hydrogen-ion concentration. Since the time of pickling is the inverse of the hydrogen-ion concentration, in order to get a direct comparison between time of pickling as actually determined and hydrogen-ion concentration, we reverse curve *B*. This gives us curve *C*. From a study of curve *C* we expect the time of pickling to be at a minimum with concentrations of acid between 18 and 25%.

Effect of Concentration on Speed of Ions

The speed at which the ions move gradually decreases as the concentration increases. This effect is particularly noticeable in concentrated solutions of sulphuric acid due to the high viscosity of such solutions. Consequently the rate of pickling at atmospheric temperatures with concentrated solutions of sulphuric acid is less than proportional to the hydrogen-ion concentration.

Significance of Electrical Conductivity of Acid Solutions

Since the electrical conductivity of an acid solution is a measure of both the hydrogen-ion concentration and the speed at which the ions move, the electrical conductivities of a series of acid solutions indicate the relative activities of the various solutions. For the two acids commonly used in pickling, these are as follows, at atmospheric temperatures:

	Conductivity						
Per cent acid	5	10	15	20	25	30	35
H_2SO_4	0.34	0.63	0.74	0.70	0.60	0.49	0.39
HCl	0.37	0.66	0.76	0.77	0.72	0.66	0.59

Since the time required for pickling varies inversely as the activity of the acid solution, by reversing these curves we get curves giving the relative times required for pickling with the various acid solutions, other conditions being kept constant. These reversed curves are shown in Fig. 2 and are found to be remarkably similar to those of Dr. Robson. It is to be noted that the effect of introducing speed of ions as a factor is to throw the minimum slightly toward lower concentrations than when hydrogen-ion concentration alone is plotted so that in this case it falls between 15 and 20% actual acid.

Effect of Temperature

Increase of temperature drives back the ionization of acid solutions slightly and thus reduces the hydrogen-ion concentration somewhat.

On the other hand, it reduces the viscosity of the solutions and thus increases the speed of movement of the ions. This effect is the more pronounced and therefore in general pickling proceeds more rapidly with heated solutions. Since the effect is mainly produced by a reduction of viscosity, it follows that heating is not important with hydrochloric acid solutions, since these are already quite fluid, but is quite necessary with sulphuric acid solutions, particularly those of fairly high concentration since these are quite viscous, and without the application of heat the movement of the ions is so retarded that the action of the acid is quite sluggish.

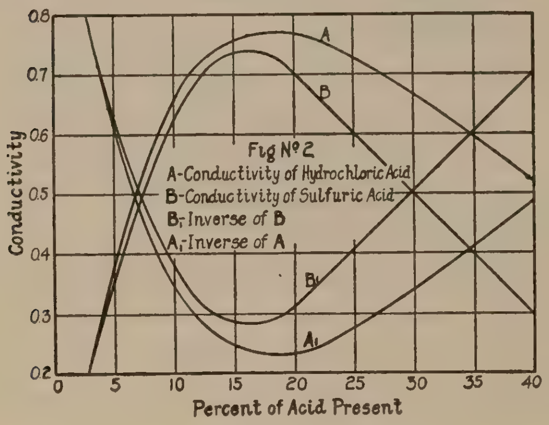

FIG. 2.

Effect of Kind of Acid

Sulphuric Acid Sulphuric acid is most commonly used due to its cheapness. The concentration employed varies from 3 to 20% actual acid. The usual operating temperatures of the bath range from 140 to 175°F (60 to 80°C). The rate of pickling with sulphuric acid is slow and the attack on the metal is pronounced. Therefore, the ware pickled with sulphuric acid is liable to be pitted. Heating of the bath is essential to maintain even a fairly rapid rate of pickling. The acid-bearing fumes rising from the hot bath are very obnoxious to workmen. In fact, it seems that the only advantage in pickling with sulphuric acid lies in the original first cost of the acid.

Hydrochloric Acid Hydrochloric acid is used in concentrations of 3 to 20% actual acid. The usual operating temperatures of the bath are from 75 to 120°F (25 to 50°C). The action of hydrochloric acid is much more rapid than that of sulphuric acid and it does not attack the iron so much or cause as much pitting of the ware. The amount of iron dissolved in the pickling operation is only about half that dissolved in pickling with sulphuric acid. This is an illustration of the principle that efficient pickling does not depend on the solution of a large amount of iron but on the solution of a very thin layer of iron directly beneath the scale, rapidly and with copious evolution of hydrogen. Since the bath is run at lower temperatures without generation of steam, the fumes are not so great in volume or so highly acid as in the case of sulphuric acid baths. The main drawback to the use of hydrochloric acid for pickling lies in its high first cost compared to the cost of sulphuric acid. Some enamelers claim that chlorides cause pinholes in enamels, but on the other hand, other enamelers claim that sulphates cause blisters in enamels.

Mixed Acids To gain part of the advantages of pickling with hydrochloric acid without incurring the disadvantage of its excessive first cost when used alone, recourse is sometimes had to the use of a mixture of hydrochloric and sulphuric acids. In general, the time required to pickle with mixed acids is intermediate between what would be required using either alone. On the other hand, in the experiments of Dr. Robson,[1] the rate of pickling is more rapid than would be calculated from the relative amounts of the two acids present and the rate at which each of them do pickling when used alone in the same concentration as that of the mixture of acids. In Dr. Robson's example 12% sulphuric acid at 120°F pickles steel in five minutes and 12% hydrochloric acid pickles steel in one minute. By simple calculation of mixtures we would expect a mixture of two parts sulphuric acid and one part hydrochloric acid having a total concentration of 12% acid to do pickling at 120°F in 3⅔ minutes. Actually it takes only 1½ minutes.

Therefore, there are decided practical advantages in the use of a mixture of acids. Whether this advantage will counterbalance the extra expense of using hydrochloric acid in connection with sulphuric depends upon the relative cost of the two acids at a given time and place.

Mixed acids are used in concentrations of 3 to 20% actual total acid and at temperatures intermediate between those used for sulphuric acid and those used for hydrochloric acid.

Formation of Salts

It is well known that the activity of a pickling bath gradually decreases even though fresh acid is added to it from time to time to bring the acidity back to the original strength. This is due to the fact that the fractional part active of any acid in solution is decreased by the presence in the solution of salts of the acid. In this case it is chiefly salts of iron that cause the retardation of activity, but any other salt of the same acid would have the same effect. Salts of other acids would cause little, if any, retardation.

Attempts are sometimes made to overcome this difficulty when hot acid baths are used by cooling the bath to remove part of the salts by crystallization. Unfortunately, the iron salts of the acids commonly used in pickling are soluble almost to the same degree in cold solutions that they are in hot ones and, therefore, the amount that can be separated out by cooling is comparatively small. It is usual practice to raise the temperature of the bath as the amount of salts in solution increases in order to get the benefit on activity of heating the acid mentioned above, and finally, to discard it when it is no longer sufficiently active at the highest working temperature.

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[1] *The Enamelist,* 3, pp. 5–8, November, 1925.

Addition of Salts

Sodium Chloride Some of the advantages of using a mixture of sulphuric and hydrochloric acids can be gained, at a very slight expense, by the addition of common salt (sodium chloride) to a sulphuric acid bath.

When common salt is added to a sulphuric acid solution it reacts with the sulphuric acid to form hydrochloric acid and sodium sulphate. The result is that we have a bath consisting of a mixture of sulphuric acid and hydrochloric acid but in addition have present a certain amount of sodium sulphate.[1] This sodium sulphate is a slight detriment in that it retards the action of the sulphuric acid to a slight extent, but this is more than counterbalanced by the increased activity of the bath as a whole due to the presence of the hydrochloric acid.

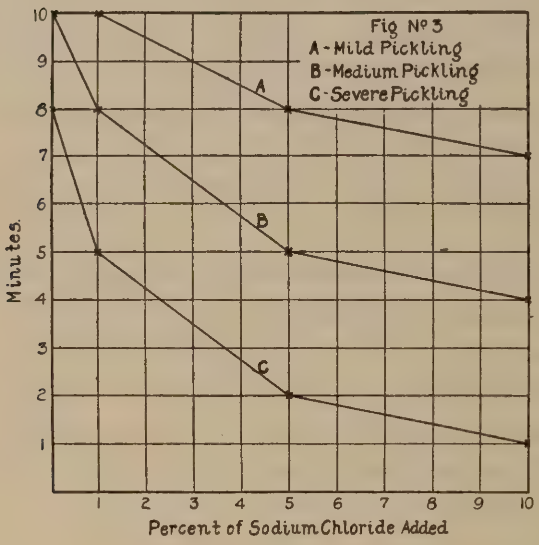

FIG. 3.

In Fig. 3 are shown the results obtained in the laboratory of the writer on adding various amounts of common salt to a sulphuric acid pickling solution. The solutions were all kept at 120°F (50°C). It will be seen that even small additions of salt have a decided effect in accelerating the action of the bath. These tests were made with fresh acid solutions but other tests made by the writer with acids containing large amounts of ferrous sulphate and with larger additions of salt have shown that the beneficial effects of the addition of salt to sulphuric acid pickling baths are quite marked at all stages in the life of the bath.

To the best knowledge of the writer, the use of salt in sulphuric acid pickling baths is not practiced at present in the enameling industry. Since it is such a cheap and handy method of increasing the efficiency of pickling baths it should be worthy of trial on a large scale.

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[1] From the standpoint of strict chemical accuracy we know that a small part of the sodium will be there as sodium chloride, but this may be neglected in this discussion.

Niter Cake Niter cake also may be used for pickling. The composition of this material varies widely, but averages about 35% sulphuric acid and 65% sodium sulphate. The acid does the pickling. The sodium sulphate not only does no pickling but when present in such very large amounts, slows down the action of the acid. Its action is exactly similar to that of ferrous sulphate in ordinary sulphuric acid pickling, and is in accord with the rule that the presence of large amounts of a salt of an acid in solutions of that acid render the acid less active.

In order to overcome this retardation in activity, it is necessary to run a niter cake bath of a given acidity at a higher temperature than a straight sulphuric acid bath of the same acidity. It is evident, therefore, that when purchased for pickling, niter cake should be paid for on the basis of its acid content and that the price for unit of acid should be less than that paid for straight sulphuric acid.

It is claimed for niter cake that owing to the fact that its action is less violent than that of straight sulphuric acid there is less pitting of the metal with its use. However, the same reduction in activity of sulphuric acid can be obtained by allowing ferrous sulphate to accumulate in the bath.

Use of Addition Agents

During the past few years the use in pickling baths of small amounts of "addition agents" or "inhibitors" has been advocated. In general, these have been sold as secret proprietary compounds. However, it is known that most of them are colloidal in nature and of organic origin. Materials that have been used for this purpose are molasses, sugars, cornstarch, spent tanning liquor, rye flour, and sulphite liquor.

Some extraordinary claims are made for the proprietary "inhibitors," the chief of these being that in some mysterious way they cause the acid to attack the iron scale and not to attack the iron. It seems inconceivable that the small amounts used could bring about such a radical reversal of the well-known action of the strong mineral acids used for pickling. It is claimed, also, that these inhibitors decrease or eliminate the formation of hydrogen. However, we can definitely say at this time that if no hydrogen is formed there will be practically no pickling. The hydrogen may be absorbed later or used up in a secondary chemical reaction but it must be formed for pickling to take place with any degree of speed.

It should be emphasized that while many of the claims made as to the action of these inhibitors have little basis either in fact or chemical theory, they do perform functions which, under certain conditions, are very desirable.

While many chemical theories have been advanced as to the action of these inhibitors, it is probable that their chief action is not chemical at all but mechanical. While they do not prevent the formation of hydrogen they do prevent it rushing up in jets and carrying with it acid vapors. The inhibitors cause a blanket of foam to form on the surface of the pickling bath and the hydrogen and steam gradually work through this blanket and pass quietly off into the air without carrying with them any acid vapors. Since both hydrogen and water vapor are in themselves odorless, tasteless, and non-irritating to human membranes, if they do not carry acid vapors they can be evolved in large quantities without being injurious or offensive to workmen.

Thus the use of inhibitors makes it possible for men to work in comfort around a pickling bath that is high in acid and which is working rapidly with consequent copious but quiet evolution of hydrogen. As we have seen, the efficiency of pickling baths increases with acid concentration up to about 20% acid. The use of inhibitors renders possible the use of such highly efficient concentrations and thus reduces the time of pickling, the acid consumption, and the amount of metal dissolved.

Another beneficial action of colloidal addition agents is that, due to certain electrical properties of all pickling baths which we need not discuss here, they tend to be deposited most heavily wherever the solution of metal is taking place especially rapidly. Thus they are deposited heavily on clean metal and around little slag spots and less heavily on spots still coated with scale. Since colloidal deposits retard solution, this selective deposition retards solution of metal where it is not needed and permits it to take place more rapidly where it is needed, that is, at spots still coated with scale. In this way excessive solution of metal, and especially pitting, is decreased.

It is evident that while the deposition of colloids is selective in that the deposits are heaviest where solution tends to be most rapid, yet deposition takes place to a certain extent at all points where pickling is taking place. Therefore, it follows that if colloidal addition agents are used in too large amounts, solution of metal will be retarded at all points and the pickling operation will be slowed down. This is probably the basis of the reports made by certain enamelers from time to time that the use of addition agents kills the action of the acid.[1] They must be used with judgment, if at all. This retardation is most liable to be noted in cases where addition agents are employed without taking advantage of the opportunity to increase the strength of the acid.

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[1] Bur. Stand., *Tech. Paper*, No. 165, pp. 12.

Effect of Electric Current

Pickling can be conducted with the use of the electric current. The effect varies according to whether the ware is made the anode or the cathode.

Anode Pickling When the ware is made the anode, the effect of the electric current is simply to accelerate the processes that take place in straight acid pickling. That is, the pickling consists essentially of the solution of a thin layer of iron beneath the scale with evolution of hydrogen. In that the current accelerates the action of the acid and assists in the rapid solution of a very thin layer of iron with copious evolution of hydrogen, it assists in producing efficient pickling.

Cathode Pickling When the ware is made the cathode and use is made of an insoluble anode, the whole pickling operation is supposed to be reversed. The flow of the current is against the solution pressure of the iron and, therefore, the solution of metal is supposed to be stopped. The acid is electrolyzed and hydrogen is deposited on the ware. This hydrogen is supposed to reduce the oxide scale to ferrous sulphate which goes into solution.

Some points in this theoretically beautiful process are questionable. It is doubtful whether the currents ordinarily used entirely stop the solution of metal and it is still more doubtful whether any great amount of iron oxide is reduced to ferrous sulphate by the action of hydrogen.

While various modifications of these two primary methods of electrolytic pickling have been proposed and numerous processes have been patented, the fact is that, notwithstanding some of the obvious advantages, electrolytic pickling has attained little commercial importance.

Absorption of Hydrogen

It is well known that hydrogen is absorbed by metals during pickling. As noted by Treischel,[1] this hydrogen causes blisters during the enameling operation. Treischel recommended the use of dilute acid solutions, 3%, to cut down the amount of hydrogen absorption. The objection to this course is that such weak acid solutions pickle slowly and, therefore, inefficiently. An optional course is to use a strong acid pickling bath, which will result in the absorption of considerable hydrogen, and then to immerse the pickled ware for a few minutes in a boiling hot water washing bath. This serves practically to free the ware of hydrogen. It is an old trick in preparing metals for plating but does not seem to be so well known in the enameling industry.

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[1] C. C. Treischel, *Jour. Amer. Ceram. Soc.*, **2**, 744 (1919).

Summary

1. Efficient pickling depends upon the solution of a very thin layer of iron directly beneath the scale, rapidly and with copious evolution of hydrogen.

2. Since the rate of pickling is proportional to the percentage of acid present multiplied by the per cent of the acid that is ionized, with the rate at which the ions move as a modifying factor, the most effective concentrations of acid lie between 15 and 20%.

3. Heating acid solutions reduces their viscosity and renders the particles more mobile, thus increasing the activity of the solutions.

4. Sulphuric acid is cheaper in first cost than hydrochloric acid, but the latter acts more rapidly and the pickling is completed with less solution of iron.

5. Additions of small amounts of common salt (sodium chloride) have a marked effect on increasing the rate of pickling of sulphuric acid baths. This is due to the formation of a corresponding amount of hydrochloric acid.

6. The chief action of addition agents is to reduce the amount of acid vapor in the fumes from pickling vats and thus permit the use of highly efficient concentrations of acid (between 15 and 20%).

7. Hydrogen absorbed by metals during pickling may be largely removed by immersing the metal in boiling hot water for a few minutes.

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GAS-FIRED ENAMELING FURNACES FOR CAST-IRON[1]

By Henry L. Read

ABSTRACT

A comparison is made of gas fired and electrically heated glass, enamel ovens. Description of equipment, data on output fuel costs, and upkeep are given.

Introduction

Some time ago a company making cast-iron bath tubs, lavatories, and miscellaneous "small ware," became curious to know whether the enamel furnace operating costs could not be improved. At that period a large number of electric resistance furnaces of a standard type were in use in the plant turning out an excellent grade of work. There were complaints, however, that the fuel bills seemed rather large and that occasional shut downs for repairs were necessary. The latter were expensive particularly because of the loss of production for four or five days while cooling off and reheating. After more than two years' use of the electric equipment, the company invited a well-known furnace manufacturer to provide something better.

There were five fuels commercially obtainable in that locality which have been successfully used for the type of work in question: coal or coke, oil, producer gas, electricity, and city gas. Since the choice of fuel is so closely connected with the kind of furnace in which it may be employed, a list is given below covering this subject for the product under consideration.

For coal or coke: muffle furnaces
For oil: muffle furnaces or intermittent furnaces
For producer gas: muffle, intermittent, or semimuffle furnaces
For electricity: Directly-heated furnaces with resistance elements along walls and arch and below hearth
For city gas: intermittent or semimuffle furnaces

The methods of operating these furnaces are well known and need no description other than the remark that with intermittent furnaces, the burners are turned off while the ware is in the working chamber and relighted while the ware is outside being sprayed, inspected, etc. These facts make the intermittent furnace unsuitable for the present work because of continual delays that are experienced while the operator is waiting for the empty furnace to come up to temperature, frequently with a sprayed tub ready to be returned for a reheat. Modern

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[1] Received June 5, 1925.

handling methods have greatly diminished the serviceability of the intermittent furnace by cutting out the delays formerly experienced during which the furnace could be reheated. The choice was therefore narrowed down except for electricity to muffle and semimuffle furnaces.

Muffle versus Semimuffle Furnaces

Other things being equal, the semimuffle furnaces are clearly more economical of heat, and of much greater importance, far less apt to get out of order. In the older types of muffles of fire clay, cracks would often develop after short periods of operation. Sometimes damage would occur from careless firing. Their life was generally short and the furnaces were frequently down for repairs. These serious objections have been largely overcome by muffles of high grade refractories which are naturally of much greater initial cost. Two years' life of a muffle is now a fair figure but the fundamental weakness is still there: the expensive muffle must be replaced at times. Consequently with similar general construction a muffle furnace is more costly to build and keep up than a semimuffle. On the other hand, a muffle insures (at least while it is new) a working chamber atmosphere entirely free of dirt and with but a small amount of products of combustion. Cheaper fuels such as coal or oil may therefore be burned since the ware will not be injured. Thus although the thermal efficiency of a muffle furnace is always lower for the same conditions than that of a semimuffle, the actual fuel cost on the muffle may be less because more refined fuels are required for the semimuffle. Therefore, the decision as to the furnace is governed not only by the cost of fuel but also by repair expense on the furnace.

To give an idea of what had been done previously, the following table was submitted:

Question of Fuel Economy As to the amount of oil to operate a suitable muffle furnace for the required work, the average seems to be around 13 gallons per hour with a minimum of 11 when turning out 60 tubs per day weighing 12,600 pounds. A low figure for oil per 100 pounds is therefore 2.1 gallons. In addition to the oil, however, the operating cost must include the price of a muffle every two years, approximately $1,000. This last statement assumes the muffles to be made of modern high grade refractories, not fire clay.

With regard to coal and coke, there is no question that a given number of heat units may be obtained from them more cheaply than from other fuels, but the lack of easy control over coal-fired muffle furnaces, the extra labor to handle them, and the more rapid deterioration of the muffles are every day causing more plants to go to oil, electricity, or gas. Loss of production on coal-fired furnaces due to

Operation	Temp.	Fuel	Firing equipment	Hrs. per day	Output per day	Fuel consumption	Unit fuel consumption	Remarks
(1) Enameling c. i. bath tubs. Fce. 8½′w.×8½′d.×4½′h. to spring (inside) semimuffle	1700°F	Nat. gas 950 B.t.u.	S.C. burners C.U. recuperators	24	60 tubs = 12600 lbs. per 24 hrs.	26700 cu. ft. per 24 hrs.	212 cu. ft. per 100 lbs.	Each tub charged cold once and reheated from 1000 to 1600°F 2½ times average. Sunday holding consumption of about 7000 cu. ft. total not included.
(2) Enameling miscel. c.i. Fce. 8′w.×6½′d.×3′h. to spring (inside) semimuffle	1600°F	City gas 500 B.t.u	S.C. burners	24	11400 lbs. small ware per 24 hrs.	37700 cu. ft. per 24 hrs.	331 cu. ft. per 100 lbs.	All ware heated once from 50 to 1600°F. Half of ware reheated twice from 1100 to 1600°F. Half reheated once from 1100 to 1600°F. Sunday holding not included 8000 cu. ft.
(3) Enameling c.i. bath tubs. Dimensions 7′w.×8′d.×3′h. to crown (inside)	1700°F	Electricity	G.E. heating elements	24	60 to 65 tubs = 12600 to 13650 lbs. per 24 hrs.	3420 to 3900 KWH per 24 hrs.	57 to 60 KWH per tub = 28.1 per 100 lbs. approx.	Same operation as (1). $1800 worth of heating elements must be replaced about every 2 years. Owner claims this is good operation.
(4) Enameling c.i. sinks. Fce. 8′6″w.×8′d.×6′3″h. to spring. Semimuffle.	1600°F	Producer gas 150 B.t.u. clean	S.C. burners	24	17100 lbs. per 24 hrs.	9070 cu. ft. per hr.	1273 cu. ft. per 100 lbs.	Each sink heated once from cold to 1600°F and twice from 1000 to 1600°F. Fces were old. Data is from 7 hr. test and does not include Sunday or lost time holding.

delays while they are regaining desired temperatures, for example, after cleaning fires, is one of their greatest weaknesses which is almost never experienced with more refined fuels. Coal was consequently eliminated from consideration.

Furnace and Fuel Adopted

After study of all the factors, city gas was recommended and adopted in this particular case. The furnace design employed is shown in Figs. 1 and 2.

The purposes kept in mind when this appliance was designed were:

1. To make it the most economical furnace in regard to fuel consumption per unit of output.
2. To make it compact.
3. To insure maximum uniformity of temperature in all parts of the actual working zone.
4. To maintain constant temperatures and furnace atmosphere regardless of the rate of working.
5. To eliminate the danger of dirt falling on the tubs.
6. In general to bring about the production of a superior grade of ware at a lower cost than could be obtained from the customer's existing electric furnaces which were admitted to be the most completely satisfactory equipment for firing enamel on cast-iron bath tubs hitherto available.

The means used to obtain these results are shown in the illustrations.

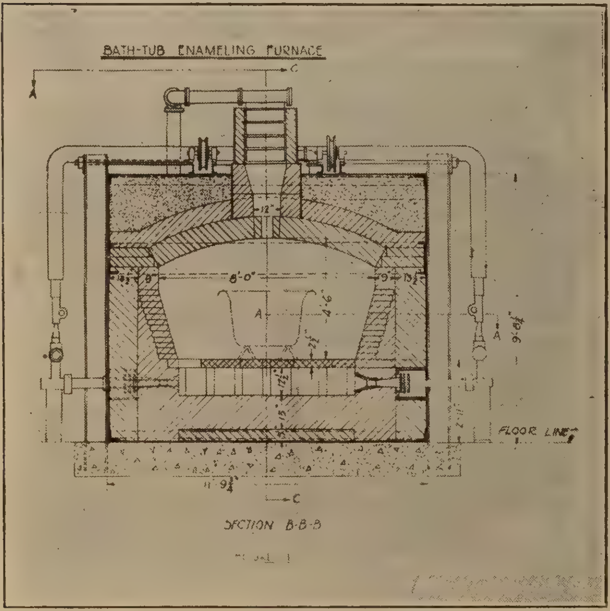

FIG. 1.

1. Economy was effected by unusually heavy insulation with Sil-O-Cel bricks and powder, 9 and 13½ inches thick; by welding the sheet steel casing to reduce internal air circulation; by the installation of standard metallic Combustion Utilities recuperators on top of the arch whereby the air for combustion was preheated approximately to 650°F and by the use of Surface Combustion low pressure velocity burners for city gas of 535 B.t.u. heat content.

2. Compactness was brought about by keeping all projecting parts such as burners, piping, door, counterweights, etc., either inside suitable recesses in the casing or behind sheet steel guards. Castings were as far as possible dispensed with.

3. Much study was involved in maintaining uniformity in temperature, resulting in the side walls being tapered as shown, corresponding to the general outlines of the tub. As will be readily appreciated, the rims being relatively light will heat more rapidly than the bottoms and therefore tend to become overheated when the furnace is run at a temperature slightly above that required in the ware. This latter condition normally exists in operation in order to make sufficiently rapid production. When the tubs are first heated from cold, the red ground coat on the rims is in danger of burning and blistering unless overheating is prevented. The scheme of keeping the brick work at an approximately uniform distance from the iron was evolved to overcome that danger. In conjunction with well-developed circulation of flue gases below the hearth, the design showed excellent results in regard to temperature distribution.

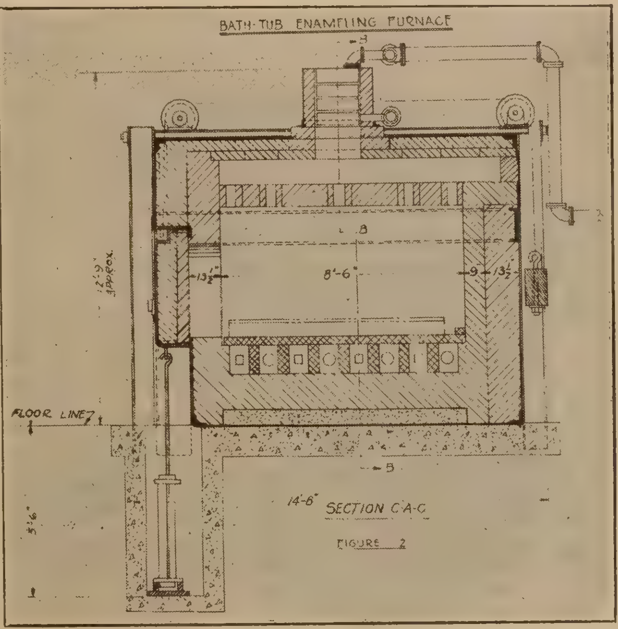

FIG. 2.

4. To meet the requirements there was evolved a satisfactory combination of the Surface Combustion automatic proportioning apparatus with the Bristol-Fuller valve and Leeds and Northrup pyrometer controller.

5. The question of particles of furnace cement, brick, etc., or occasionally unburned carbon, getting into the white enamel during the firing, was considered a most serious one. To get around it, the door was constructed so that it was lowered to open, the converse of ordinary procedure in which the door is closed by being lowered. Thus trouble from little pieces falling from the door upon the work as the latter was inserted into or withdrawn from the heating chamber was avoided. Furthermore, the furnace interior was covered with a special "Bristol" glaze which protected the ware from dirt particularly during the firing. The danger of unburned carbon was removed by setting the inspirator adjustment so as to maintain always an excess of oxygen. Perfect mixing and firing was provided for by the Venturi throats and the tunnels at the burner outlets.

6. It was felt that if the five points previously mentioned were thoroughly covered, superiority of ware necessarily would follow pro-

vided that sound principles of furnace construction were followed. It is gratifying to note that these expectations were entirely fulfilled.

Prevention of Reduction

A certain amount of prejudice at the start had to be overcome because of the fear that in the absence of a muffle black specks of unburned carbon from the fuel might settle on the ware in the furnace and so ruin its appearance. Likewise there was the danger of burning the ground coat if the atmosphere through some mischance should become reducing.

Eventually it was clearly demonstrated that with around 50% or more excess air there was not the slightest danger of spoiling the tubs from chemical reactions or floating dirt specks. Even the loudest objector admitted finally that the muffle had been proved to be unnecessary. But further than that, it ultimately was shown that the appearance of the tubs heated in the presence of products of combustion with an appreciable excess of air was markedly superior to that of tubs from the electric resistance furnaces.

Cost of Operating

Thus the first of the main features of the furnace of interest to the customer was covered: namely, that the work could be done better in it than in the electric furnaces. The second was whether the cost would be greater or less with gas than electricity. On this point, only cost data kept over a considerable period are of real meaning, but the preliminary figures obtained are interesting. It was found that roughly 70 tubs weighing 220 pounds each per 24-hour day can be made in this furnace with a consumption of about 42,000 cubic feet of gas. This is equivalent to 600 cubic feet per tub or 273 cubic feet per 100 pounds. In addition about 8,000 cubic feet are needed to heat the furnace after the week-end shut down. Allowing for the various operating delays, the furnace produces in one week 365 tubs weighing 220 pounds each on 240,000 cubic feet.

The cost of electric enameling includes the wages of a switchboard operator 24 hours a day, as well as approximately 50 kilowatt hours per tub. It does not, however, allow for rejections but refers merely to the total number of tubs of the specified size put through the furnace as does the figure for the gas furnace.

Rejections

On the question of rejections, the records showed that there were certainly no more defective tubs from the gas furnace than from the electrics and probably not as many.

Labor

Labor for operating the two types was the same except that one switchboard operator for the entire battery of electric furnaces was required at all times. No man corresponding to him is necessary on any number of gas furnaces.

Repairs

As to repairs, the gas furnace shows a great superiority. The electric furnaces give continual trouble on this score, involving not only actual labor and material for each breakdown (a comparatively small part of the expense usually), but also the loss of production for about five days and the expenditure of energy to heat the furnace up again to working temperature. The original electric furnaces at the plant were objectionable because the resistors were set in the side walls where they frequently were broken by contact with the fork carrying tubs into and out of the furnace. To get around this, there were built, with the advice and assistance of the industrial heating department of a large maker of electric appliances, a number of improved furnaces that were supposed to be the last word in perfection. The resistors in the new furnaces were placed in the arch and below the hearth for protection. Unfortunately the altered design has not shown any reduction in the frequency and cost of repairs.

Size of Ware

Up to this time only one size of tub has been referred to: the one which was 220 pounds and 5 feet long. It should be understood also that all kinds of tubs were successfully heated in the gas furnace including those 6½ feet long weighing over 400 pounds and having aprons on one side and one end. These last are most difficult to heat properly because of the great unevenness of the distribution of the weight.

Output

Although all the data collected thus far led to the belief that the overall cost of heating by gas would be well under the cost with electricity, the extremely important question of capacity and rate of heating in the gas furnace still remained open. The output of 70 tubs of 220 pounds each per day at 1790°F previously mentioned was as fast as the crews could be made to work on steady production with either type under present conditions, but there was always the possibility that labor-saving devices might enable the men to increase the output. Furthermore, improved enamels might require a somewhat higher temperature than is now employed. With these facts in mind the electric furnaces had been built and subjected to very special speed tests which it was necessary that the gas furnace should at least equal before it could be considered satisfactory. Consequently, arrangements were made to try out the gas furnace for rapidity of working just as the electric furnaces were tested.

Going over the records it was found that the best performance of any of the electrics was an output at the rate of 35 tubs in 8 hours at 1820°F. This is equivalent to one tub every 13 minutes and 42.8 seconds. Under corresponding conditions the gas furnace averaged one tub in 13 minutes and 22.5 seconds at 1825°F. The capacity of the gas furnace was therefore superior to that of the electrics.

Heat Balance

A heat balance of the gas furnace follows:

Heat absorbed in work	28.3%	Heat lost in the flue gases leaving open door	1.6%
Heat lost in wall radiation	14.1%	Heat given up to air in recuperator	30.9%
Heat lost in open door radiation	2.4%		
Heat lost in flue gases leaving recuperator	22.7%	Total	100.0%

The tests described in the foregoing have clearly shown that the Surface Combustion gas furnace has marked advantages over the electric furnaces at the plant referred to in regard to quality of product, reserve capacity, and overall cost of the firing operation per unit of output. An order recently given by the user for four more similar furnaces is sufficient proof of this.

THE SURFACE COMBUSTION COMPANY
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NEW YORK CITY

DEFECTS IN ENAMEL DUE TO CAST IRON

By A. Malinovszky

ABSTRACT

Microphotographic examination of iron on which enamel has pinholed, blistered, and come perfect are cited as evidence that carbon is practically the only agent in cast iron causing blistering and pinholing and that it is the condition and not the presence of carbon that causes these defects.

The real cause of pinholing and blistering is a question that frequently confronts the enamelist and each time that this trouble occurs, the conditions seem to vary. However, the solution for each repetition of this trouble seems to narrow down to quite a small range of causes. Positive answers to many of the questions concerning pinholing and blistering will be a great accomplishment.

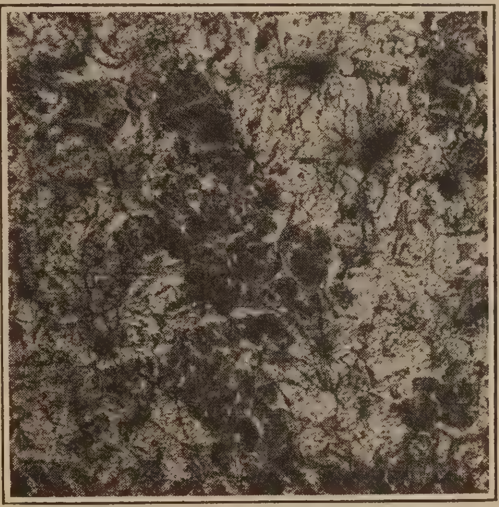

Fig. 1.—100×.

Broadly considering the cause of blistering and pinholing in enameled ware, we find many factors which can be roughly grouped into three classes; (1) defects due to raw materials or volatilized matters in ground coat or enamel, (2) those resulting from working conditions, and (3) from the iron.

Naming briefly the causes of our troubles in emameling sanitary cast-iron ware, we have:

1. Dirty iron or uneven thickness, or iron containing slag.
2. Iron containing high phosphor, sulphur, manganese, and carbons, especially when the latter is in segregated forms.
3. Heavy or overfired ground coat.
4. Improperly dried ground coat.
5. Too rapidly applied enamel or "pilling" it in spots.
6. Foreign matters in the enamel, or wrongly compounded.
7. Underfused enamel, ground coat, or furnace gases.

Effect of Carbon Content in Iron

For a period of several months an accurate check was kept on each raw material and record kept as to the results obtained after the slightest changes in materials, equipment, working conditions, and methods were made. All known results obtained by different experts were used in experiments with varied results. Samples from castings and microphotographs were sent to different well known metallurgists. The final answer resulting from these studies was that the trouble lay in the uncertain carbon content in the iron.

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[1] Received April 6, 1926.

[1] The letters in the microphotographs designate the following: P, pearlite; S, steatite; F, ferrite; MnS, manganese sulphide; G, graphite; and M, martensite.

Reduction Due to Carbon and Iron Tin oxide and antimony oxide used in the enamel mix are easily reduced by carbon. The oxidizing action of the iron during the enameling process forms carbon gases. These not only are liable to produce blisters but also to reduce the opacifying agents so that they appear as black specks in the enamel.

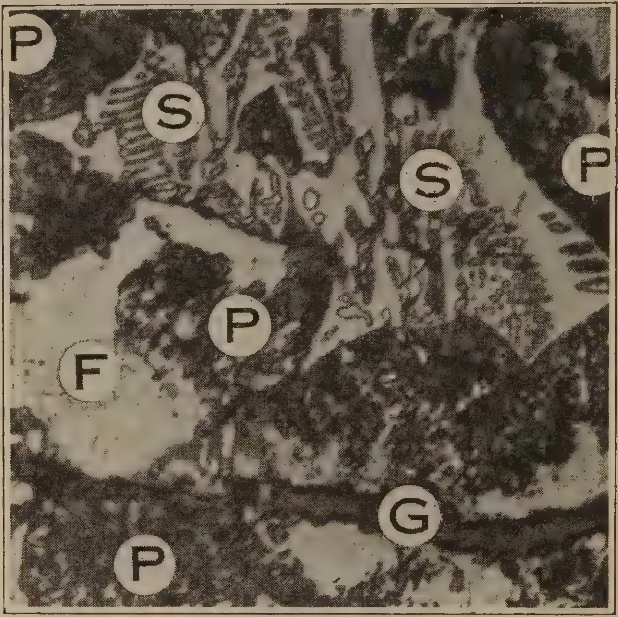

Fig. 2.—1000×.

The sulphur, phosphor, manganese, and silicon contents of the iron were varied in countless proportions with no avail. Steel scrap and different cokes were experimented with and no satisfactory results were obtained. It was not until an entirely different pig iron was used that the carbon content of the iron was brought under complete control. A noticeable difference was observed in the working of the ware.

In the many heating and cooling processes the carbon rapidly changes in chemical and physical properties. Pinholing and blistering may occur due to the volume changes of gases contained and formed in the iron.

How to Keep Carbon Low The chemical affinity of carbon for iron is very great but iron discharged rapidly from a cupola and at proper temperatures will not be anywhere near its saturation point in carbon. Iron allowed to remain in a cupola for a long time at low temperatures will contain carbon close to its saturation limit. Iron having been for a considerable time in contact with the cupola coke will naturally have absorbed its limit of carbon. The natural tendency will be for this carbon to be present in several different crystal forms many of which are undesirable and injurious.

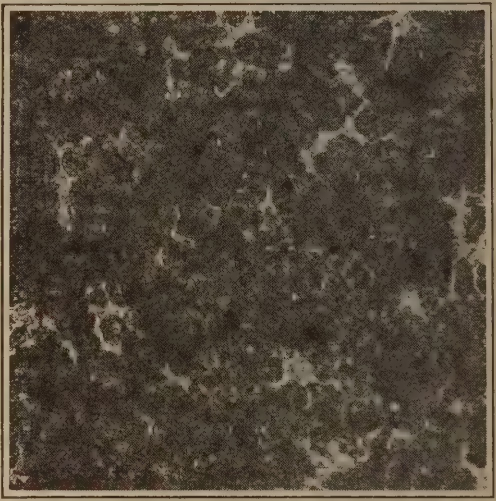

Fig. 3.—100×.

Pig irons must be mixed in certain proportion and with scrap before good results can be obtained. This mixing is necessary because some irons have greater affinity for carbon in the cupola than have others.

The constitution and properties of iron used in enameling are far more difficult to understand than are those of steel. The difficulty of predicting from an analysis the effect of any change in composition of cast iron is far greater. A change in any of the constituents of cast iron is liable to effect changes in several other ingredients.

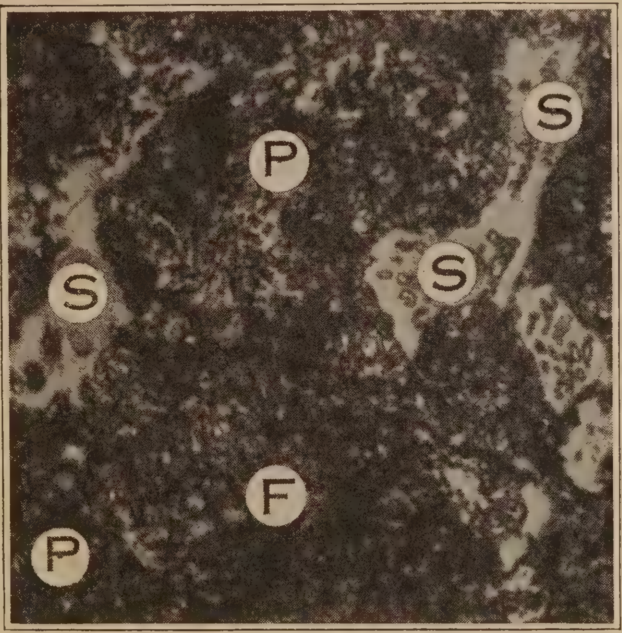

FIG. 4.—1000×.

Value of Chemical Analysis of Cast Iron

Two different cast irons having almost identically the same chemical analysis when enameled with the same ground coat and enamel in the same temperature will give different results. Cast irons with extreme differences in their constituents have given equally good results. Chemical analysis will not always show the causes of pinholing and blistering. More stress should be placed on the state of the elements in cast iron rather than their proportion as shown by a chemical analysis.

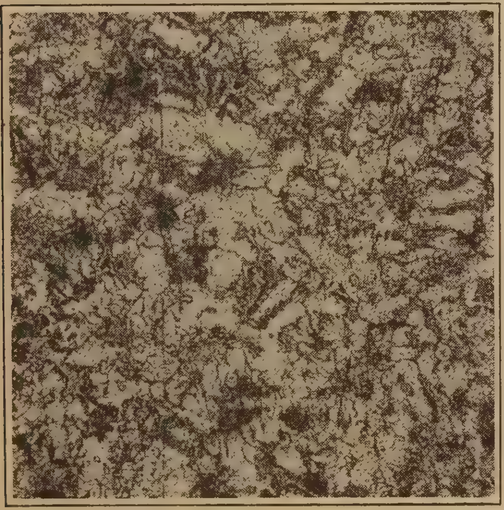

FIG. 5.—100×.

The microphotographs of Figs. 1, 2, 3, and 4 were all taken from one specimen from a bath tub which was badly blistered or broken out. Figures 1 and 2 were both taken from the same end of the specimen; Figs. 3 and 4 were taken from the opposite end of the sample where no blisters were present on the enameled surface. This sample shows a different structural composition at the two ends. Figure 1, 100×, shows the general structure at one end. Figure 2, 1000×, same as Fig. 1, shows detail of the materials present, *i.e.*, steatite, graphite, pearlite, ferrite, and manganese sulphide.

Figures 3 and 4 show the general structure of the other end of the sample. Figure 3, 100×, shows no free ferrite, a smaller amount of graphite, and much more pearlite than the other end of the sample. Figure 4, 1000×, same as Fig. 3, shows a structure consisting almost wholly of pearlite and steatite with a small amount of graphite.

The above analysis of the sample is as follows:

Compounds Present

	Per cent		Per cent
Total carbon	3.245	Graphitic carbon	3.24
Graphitic carbon	2.808	Iron carbide	6.25
Combined carbon	.437	Manganese carbide	.32
Silicon	2.516	Iron phosphide	4.49
Manganese	.391	Iron silicide	7.53
Phosphor	.662	Manganese sulphide	.15
Sulphur	.055	Iron	78.02

Structural Composition

	Per cent		Per cent
Pearlite	52.56	Manganese sulphide	0.15
Steatite	2.62	Ferrite	37.87
Graphite	2.80		

Figures 5 and 6. This sample was cut out from the opposite end of a bath tub on which no blistering occurred during the enameling process. The sample shows the same structure to be present at both ends.

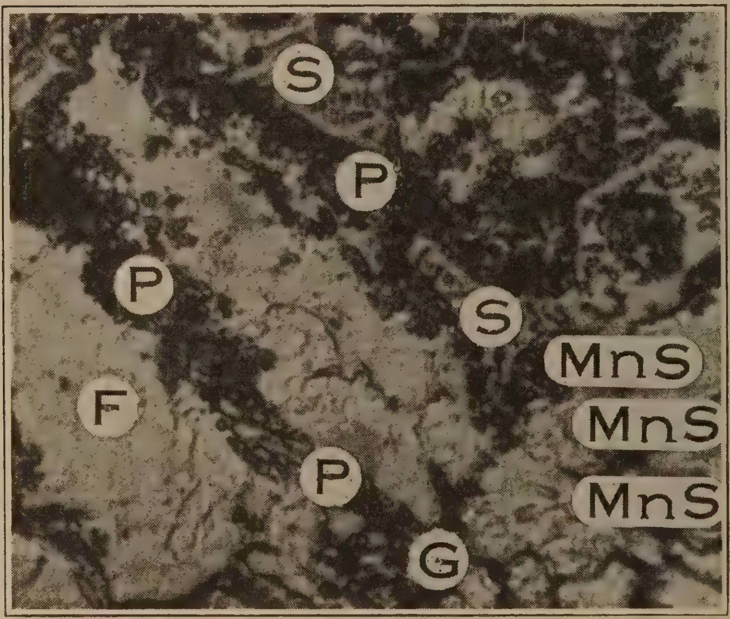

Fig. 6.—1000×.

The microphotograph, Fig. 5, 100×, shows the general distribution of materials. The microphotograph Fig. 6, 1000×, same as Fig. 5, shows under the microscope much less pearlite than the analysis would call for.

This sample has the following analysis:

Compounds Present

	Per cent		Per cent
Total carbon	3.191	Graphitic carbon	3.19
Graphitic carbon	2.808	Iron carbides	5.49
Combined carbon	.383	Manganese carbide	.25
Silicon	2.887	Iron phosphide	4.88
Manganese	.526	Iron silicide	8.66
Phosphide	.721	Manganese sulphide	.23
Sulphur	.088	Iron	77.30

Structural Composition

	Per cent		Per cent
Pearlite	45.92	Manganese sulphide	.23
Steatite	7.21	Ferrite	43.84
Graphite	2.80		

In Fig. 7, 1000×, the original pearlite areas were apparently changed to martensite. These areas, which appear dark in the photograph, are in reality yellow under the microscope. No blistering occurred when the enamel was applied to this iron.

Figure 8, 1000×, shows large areas of ferrite and more steatite than does Fig. 7. This sample was taken from a blistered sink.

Figure 9, 1000×, shows a slight trace of steatite. This sample was taken from a tub on which no trouble was experienced in enameling.

Figure 10, 1000×, shows large ferrite areas and less graphite. This sample was taken from a bath tub on which the enamel showed pinholing and in patches looked pitted.

Figure 11, 1000×. Martensite is very prominent. This sample was taken from a bath tub which blistered so badly as to leave the enamel full of minute pinholes.

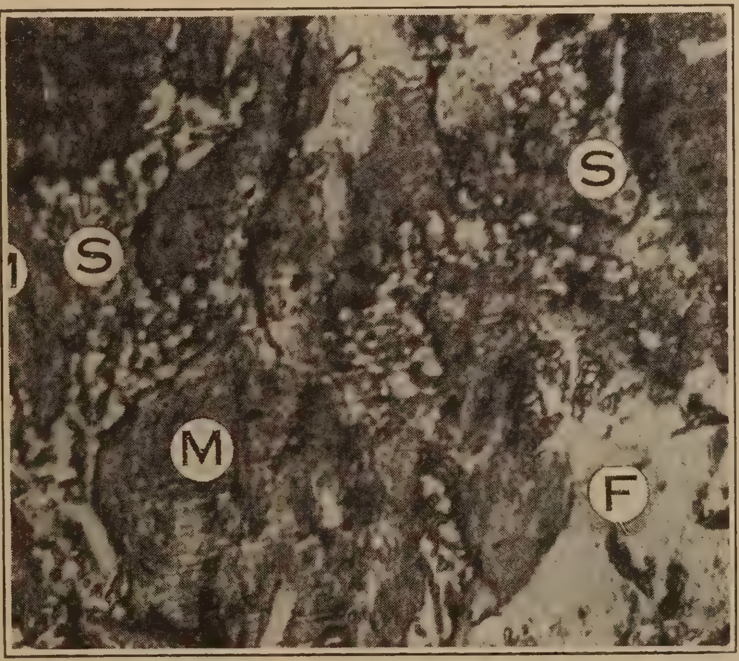

Fig. 7.—1000×.

Figure 12, 1000×. The graphite occurs in entirely different form than it does in the other samples. This sample was taken from a bath tub where blistering was prominent in patches.

Figures 13, 14, and 15 were taken from a bath tub which was covered with large and small pinholes. These samples as seen in the microphotographs possess a most remarkable structure. They appear to consist entirely of straight ferrites with slag veinlets. This condition is found to be constant throughout the sample.

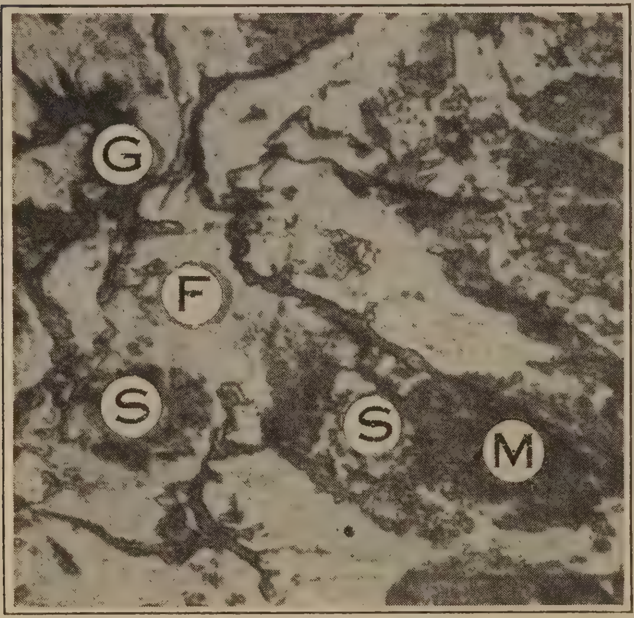

Fig. 8.—1000×.

There is no trace of the usual structural elements of cast iron as used for enameling; that is, pearlite, steatite, and graphite, etc. Some of the black spots are silicate material and contain what apparently are areas of graphite.

Figure 13, 100×, is an unetched sample showing the structure of the sample and the distribution of the slag veinlets. This sample was taken from the bottom of a bath tub which was covered with pinholes.

Figure 14, 100×, unetched, shows a structure of black spots on the surface. This figure has a very unusual appearance. No reason can be seen for the structure. The tub from which this specimen was taken had been subjected to repeated heating in an effort to patch both large and small groups of blisters or "glass eyes" which occurred during the enameling operation. Some of these blisters were black.

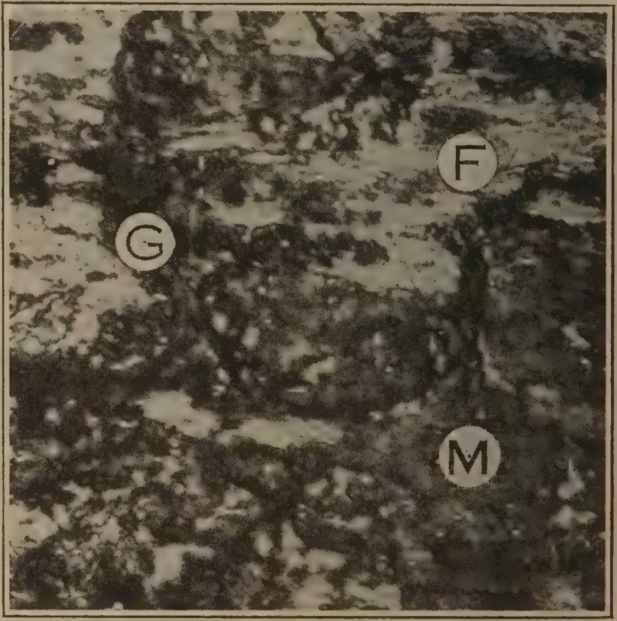

Fig. 9.—1000×.

The numerous heatings (16 times) have developed brittleness of the iron which under the microscope has the appearance of an over-fired structure.

Figure 15, 1000×, which was etched with HNO_3 in alcohol shows details of ferrite and veins of slag material. The slag under the microscope seems to be composed of two different materials having slightly different colors. The graphite spots also are noticeable owing to their odd form.

A very prominent metallurgist who examined these photos said: "In my experience, I have never run across a specimen in any way similar to this one."

Figure 16, 1000×, is a photo of one of the blotches where the enamel broke out very badly. Every metallurgist who has examined this photo claims he cannot comprehend it.

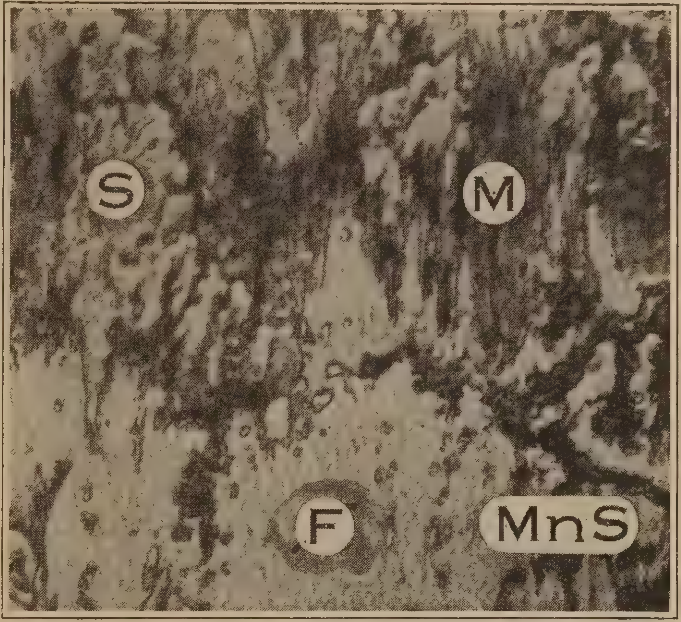

Fig. 10.—1000×.

In reviewing the preceding microphotographs and comparing them with the results obtained from these samples during the enameling operation it is very difficult to draw any definite conclusion as to the cause of blistering in enamel on cast iron merely by comparing one photo with another. In Figs. 13 and 14 the cause of the blistering and pinholing of the enamel is shown very clearly.

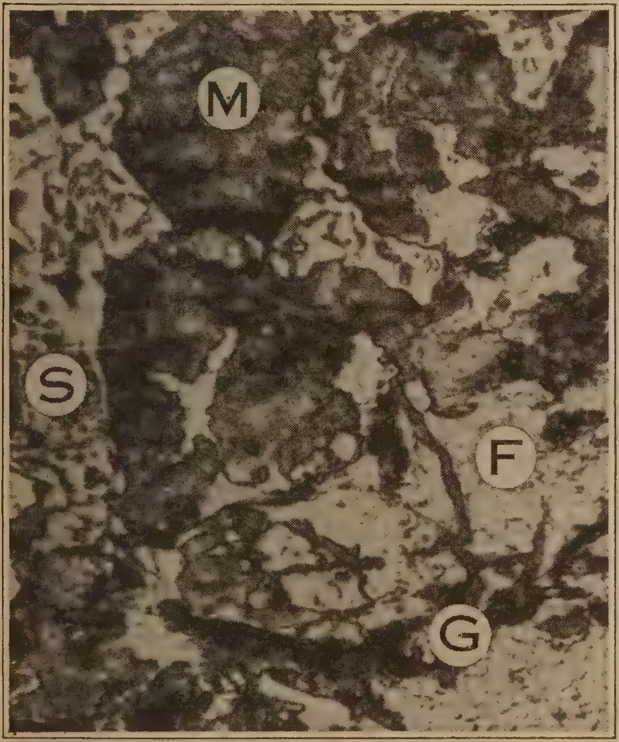

Fig. 11.—1000×.

Enamel Defects Due to Condition of Carbon

It is my belief that pinholing and blistering are due to the condition of the carbon in the iron and not due (as many insist) to the presence of carbon.

Cast iron cannot be considered a simple metal or alloy. It is an aggregated compound of various structures. Even the slightest change in the proportion of the compounds in the pig will, upon melting, change the character of the iron so much that it becomes a product of different qualities and with different expansions.

What may seem to be a slight chemical change of the primary mixture of the iron, may be the fundamental cause of an enamel chipping, crazing, or blistering when it is applied to the ware.

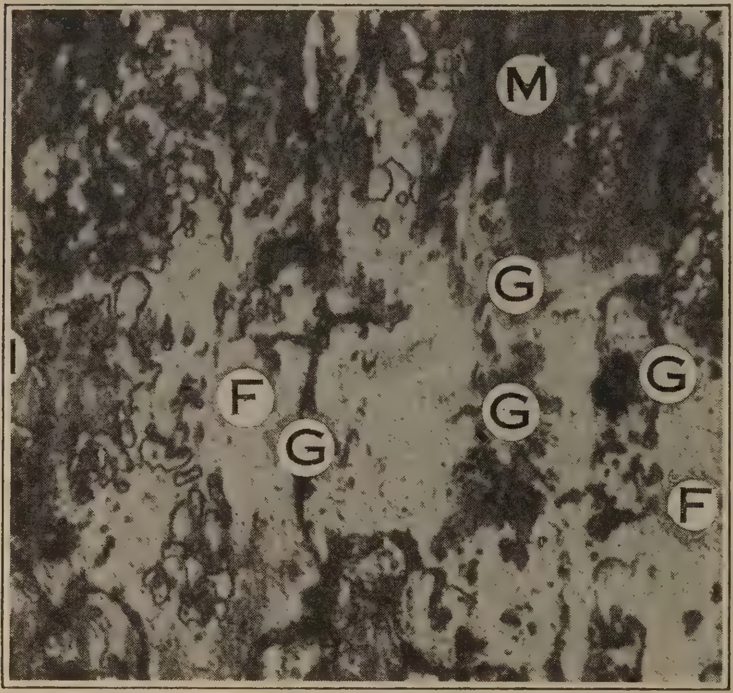

FIG. 12.—1000×.

Effect of Other Constituents

If blistering and pinholing of enamel in cast iron are caused by the iron this is the only explanation so far at hand. We cannot overlook the influence on the enamel of phosphor, sulphur, manganese, and other impurities collecting into localized groups, nor that of manganese sulphide known to the foundrymen as "hot spot." Many "hot spots" have been found so extremely hard that no tool will cut them and upon application of enamel a craze will appear resembling a spider web. The occurrences of this phenomenon are more frequent in bath tubs than in similar castings.

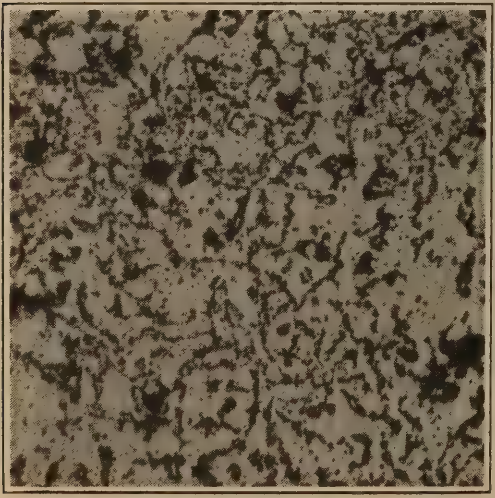

FIG. 13.—100×.

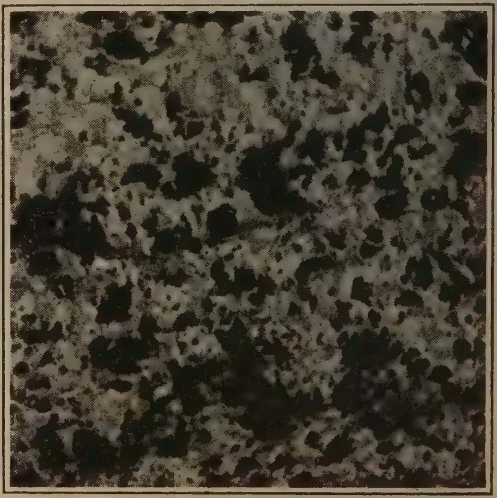

FIG. 14.—100×.

High silicon content in an iron causes considerable damage since it precipitates the carbon, driving it out of combination into a graphite form. The iron is thus changed from ferrite and pearlite into ferrite and graphite. This is illustrated in Figs. 13 and 14.

The microphotographs have shown no pearlite to be present in cast irons having high silicon and low sulphur and manganese. Silicon in cast iron seems to prevent the formation of iron carbides and promotes ferrite and graphite only.

The foregoing conclusions have been previously advanced in slightly different aspects by the author in 1917, when, working in conjunction with Mr. Hathaway, metallurgist, an article illustrated by lantern slides was presented before the American Chemical Society Local Section of St. Louis, Mo. A paper by the author[1] drew attention to the variation of the carbon in the castings analyzed before and after the ware was enameled.

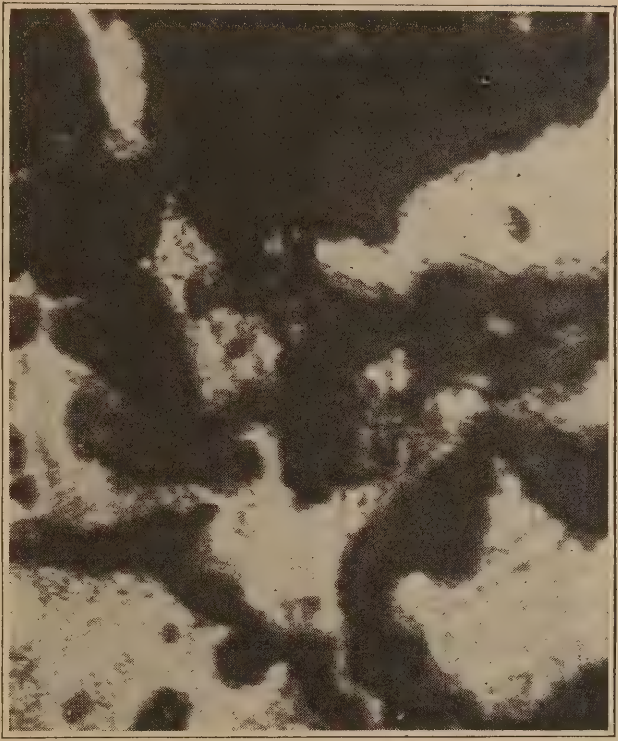

Fig. 15.—1000×.

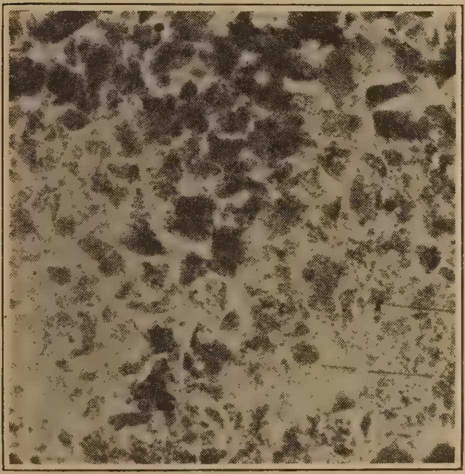

Fig. 16.—1000×.

It would seem to be convincing testimony that carbon is practically the only agent in cast iron that will cause blistering and pinholing due to its continuous transformation from one state into another during the enameling process.

Washington Iron Works
Los Angeles, Calif.

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[1] A. Malinovszky, "Enameling Defects Due to Cast Iron," *Jour. Amer. Ceram. Soc.*, **8** [1], 72–78 (1925).

SEVERAL GAS EXPANSION POROSIMETERS[1]

By A. Ernest MacGee[2]

ABSTRACT

A relatively inexpensive and simple brick porosimeter and its operation is described. A convenient indirect and a direct reading porosimeter for small test pieces is described. The direct reading porosimeter reduces calculations to the minimum.

Gas Expansion Method

In an effort to overcome the objections inherent in the liquid absorption method, Washburn and Bunting[3] developed several types of apparatus which make use of the principle of gas expansion for determining porosity. In this method, a gas instead of a liquid is used to fill the pores of the sample, its amount being determined by measuring the change in pressure which accompanied a definite increase in its volume. From the pressure differences obtained by any one of several general procedures, it is possible to calculate either the solid or the pore volume of the test piece. Bulk volume is determined by direct measurement or by liquid displacement. The gas expansion method yields very accurate results even for bodies of low porosity and exceedingly fine pores.

Although Washburn and Bunting developed an apparatus of the McLeod-Gauge type, it remained for Navias[4] to arrange this type of apparatus into a sturdy convenient form in which the pore volume is read direct. However, the bulk volume must be determined in some second apparatus, an obvious disadvantage.

The Direct Reading Porosimeter

In the following apparatus based upon the principle of gas expansion, both the bulk and solid volumes are directly read from burettes. This simplifies the calculation to a single subtraction and division, thus greatly facilitating the ease with which a complete porosity and apparent specific gravity determination can be carried out.

Figure 1 is a diagrammatic sketch of the apparatus. The sample container, *B*, is of exactly 100 cc internal volume from *A* to *Z*, (being about 4¾ in. long and 1¼ in. in internal diameter). The expansion chamber, *C*, is an ordinary 100 cc burette, the 100 cc mark being at *Z*. *D* is a burette of about 200 cc capacity. Only the lower portion of this burette need be calibrated, the 100 cc mark being at *F*. *E* is an ordinary meter stick calibrated in millimeters for measuring differences of pressure in *C* and *D*. *G* is a flexible metal covered rubber tube. It is necessary that the tube be metal covered because of excessive error caused in stretching of the rubber tube by the mercury which is essential to the use of this type of apparatus.

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[1] Published by permission of the Director, U. S. Bureau of Mines. Received July 26, 1926.

[2] Coöperative Research Engineer, U. S. Bureau of Mines.

[3] E. W. Washburn and E. N. Bunting, "Porosity VI. Determination of Porosity by the Method of Gas Expansion," *Jour. Amer. Ceram. Soc.*, **5**, 112 (1922); "Porosity VII. The Determination of the Porosity of Highly Vitrified Bodies," *Jour. Amer. Ceram. Soc.*, **5**, 527 (1922).

[4] L. Navias, "Metal Porosimeter for Determining the Pore Volume of Highly Vitrified Ware," *Jour. Amer. Ceram. Soc.*, **8**, 816 (1925).

Theory of Operation Assume that mercury is standing in the burette *C*, up to the point *Z*. On closing the stop-cock, there is enclosed in *B* exactly 100 cc of air. If this 100 cc of air be expanded until it is 200 cc by allowing mercury to run out of *C*, the difference in pressure between the mercury column in *C* and *D* will be one-half of atmospheric. Obviously, if any volume of air in *B* is expanded until the pressure difference of the mercury column in *C* and *D* is one-half of atmospheric, the volume of air in cubic centimeters contained in *C* will be equal to the volume of air originally in *B*, that is, halving of the pressure doubles the volume.

With a sample in place in *B*, a certain portion of the total volume is occupied by the solid part of the sample. Thus, setting the mercury at *Z* and closing the stop-cock, an unknown volume of air is enclosed in *B*. On expanding this volume until the pressure is one-half of atmospheric, the volume of air in *C* is the air volume in *B* unoccupied by solid material. By subtracting this volume from 100 (the total volume of *B*), the solid volume of the sample is obtained. That is, if there were 40 cc of air in *C*, the solid volume would be 100 minus 40, or 60. However, with the 100 mark at *Z*, 40 cc of air would be in *C* when the reading of the burette was 60. Thus, the burette reading on *C* is the solid volume of the test piece.

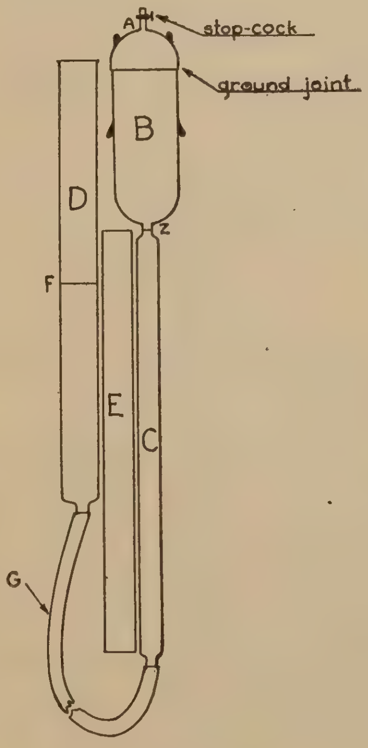

FIG. 1.

Assume sufficient mercury is placed in the apparatus to cause the levels to be at *F* and *Z* when they are held parallel. With the previously mentioned sample in *B*, its bulk volume is determined by allowing mercury to flow from *D* until *B* is filled to the point *A*. Assume that

20 cc ran out of D. Then 100 minus 20, or 80 is the bulk volume of the sample. With the calibration of D beginning with 100 at F, the burette would read 80 when 20 cc of mercury had run out. Thus the burette reading on D is the bulk volume of the test piece. On subtracting the solid volume from the bulk volume and dividing by the bulk volume, the percentage porosity is obtained by multiplying by 100.

Determining of Porosity Sufficient dry and clean mercury having been previously placed in the apparatus to cause the levels to stand at Z and F, the sample is placed in B and the cover clamped tight by means of rubber bands.

(1) With the stop-cock open, D is elevated until the mercury level in C stands at Z, after which the stop-cock is closed.

(2) By lowering D, mercury is allowed to run out of C until the pressure difference between C and D is one-half of atmospheric as read on E.

(3) The burette C is read, this reading being the solid volume, s, of the test piece.

(4) The stop-cock is opened and D is elevated until the mercury level in B stands at A.

(5) The burette, D, is read, this reading being the bulk volume, b, of the test piece.

(6) Porosity in per cent $= \dfrac{b-s}{b} \times 100$

If apparent specific gravity is desired, the solid volume, b, is divided into the dry weight, w, of the test piece, the quotient being the value sought.

Accuracy The precision attainable with this method depends largely upon the refinement of construction of the apparatus. The apparatus herein described was not designed to give the maximum attainable accuracy. Rather, it was so constructed as to employ rectangular test pieces which could later be used in cross-breaking strength or other tests and to give quite reliable values for all ceramic bodies, other than those of porosities below about 5%. In order to determine the extent to which results could be duplicated from time to time, porosity was determined on the same test piece at four different times with the following results:

Test	1	2	3	4
Per cent porosity	35.0	35.3	35.2	35.3

Accuracy can be increased by employing test pieces which fit snugly into the apparatus and by refining the calibration and size of the burettes, C and D, as well as the method of obtaining the differences in pressure. Like all of the air-expansion methods, slightly larger porosities are usually obtained than by the liquid absorption method.

In order to obtain a comparison of the results rendered by the direct reading, indirect, and water methods, the porosity of a number of test pieces was determined by each of these methods. The results are tabulated in Table 1.

TABLE I

PER CENT POROSITY

Test piece	Direct reading	Indirect	Water
1	34.5	34.3	31.9
2	35.0	34.9	32.2
3	39.9	39.2	37.2
4	33.7	31.8	32.1

The Indirect Method

An apparatus was designed to operate on the general principle in which the free air space is calculated after measuring the fall in pressure which accompanies a definite increase in volume. This type of apparatus was constructed in order that porosity and apparent specific gravity could be accurately and conveniently determined for test pieces of a wide range in size and shape. This apparatus was designed to carry a test piece 1 x 1 x 4 inches, a convenient size to make and a size which readily lends itself to other tests, including cross-breaking strength on a 3-inch span.

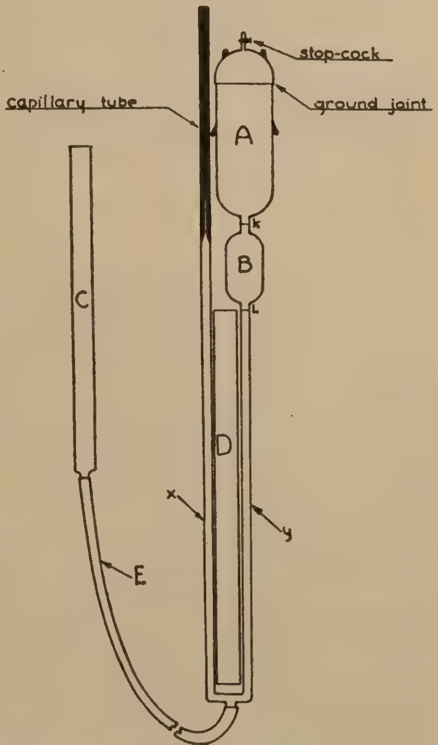

FIG. 2.

Description of Apparatus

Figure 2 is a diagrammatic sketch of the indirect reading porosimeter. *A* is the sample container of any convenient volume up to the mark, *K*. In this particular apparatus, the volume of *A* is 145 cc, the cylinder being about 5 inches long and $1\frac{1}{2}$ inches in diameter. This is a convenient size for carrying 1 x 1 x 4 inch test pieces and at the same time allowing for considerable oversize. *B* is an expansion bulb of any convenient volume from *K* to *L*. With a sample container of the volume mentioned above, about 50 cc is the proper volume of *B* in order to assure accuracy when a great variety of sizes in test pieces are likely to be encountered. *C* is a regular 200 cc burette calibrated into tenths. *D* is an ordinary meter stick. The open end manometer, *x* and *y*, is made of about 5 millimeter bore tubing. Beginning at a point just below *K*, the open end of *x* is made of fine capillary tube. This is in order to avoid the use of a second stop-cock and at the same time to retain accuracy in the bulk volume measurement (as A is being filled with mercury, some would be running out of C into this manometer tube, thus making the reading on C too large). E is a metal covered rubber tube, metal being used to avoid stretching by the mercury employed in the apparatus.

Determining of Porosity Sufficient mercury having previously been placed in the apparatus to fill C to the zero mark when the mercury level stands at K, the sample is placed in A and the top fastened securely by means of rubber bands.

(1) With the stop-cock open, C is elevated until the mercury level in B stands at K.

(2) After closing the stop-cock, C is lowered until the mercury level in B stands at L.

(3) The pressure difference between x and y is read on D. The solid volume is calculated from this reading.

(4) After opening the stop-cock, C is elevated until the mercury level in A stands at the stop-cock.

(5) C is read. This reading subtracted from the total volume of A gives the bulk volume, v, of the test piece.

Calculating Solid Volume (1) The reading, R, of D (as determined under 3 above) is subtracted from the barometric pressure in order to obtain the pressure, p, after the expansion process described under 1 and 2 above.

(2) Air space, a, in $A = \dfrac{p \times B}{R}$

B is the volume from K to L

(3) Solid volume, s, of test piece $= A - a$

A is the volume from the stop-cock to K

(4) Porosity in per cent $= \dfrac{v - s}{v} \times 100$

If apparent specific gravity is desired, it is determined by dividing the solid volume into the dry weight, w, of the test piece.

Advantages This apparatus is rugged and simple in its construction. It gives quite accurate values for all classes of ceramic bodies other than vitreous, on test pieces of wide variation from the general size 1 x 1 x 4 inches. Where many tests are being made, the mercury soon becomes dirty unless exceptional care is used to clean the test pieces before using. This apparatus is relatively insensitive to the small amount of dirt which gradually accumulates in any apparatus of this general type. Although this apparatus does not have the advantage of the direct reading feature, it is quite rapid and convenient in its operation.

Accuracy The accuracy attainable with this apparatus is all that can be necessary except for ware of the lowest porosities. For great accuracy, it is essential that the rubber tube does not stretch.

This is assured by having it enclosed in a snugly fitting flexible metal tube.

Indirect Reading Brick Porosimeter

Although Washburn and Bunting first described the general procedure and type of apparatus used in determining porosity values on commercial size brick by the air expansion method, it remained for Bole and Jackson[1] to modify and develop this method into a convenient and accurate means of determining porosities on standard size brick. In order to overcome the disadvantages of the inclined gage and glass containers used by Bole and Jackson, Pressler[2] developed an all-metal apparatus which made use of a simple vertical manometer. A slight modification of this apparatus has been in use in the Bureau of Mines laboratories for the past four years with quite satisfactory results. In each of these methods, solid volume is calculated from the pressure difference obtained after a definite expansion had taken place. Owing to the small bore manometer tubing used, a troublesome amount of tapping is required in order to assure that the mercury has come to equilibrium. Each of these methods called for the use of a motor driven vacuum pump as did that described by Hartmann, Westmont, and Morgan.[3] This of course adds greatly to the first cost of the apparatus as well as the inconvenience and expense of its operation. A water pump could be substituted with doubtful satisfactoriness. Although Pressler, and Bole and Jackson determined the bulk volume of the brick by direct measurement, Hartmann, Westmont, and Morgan introduced the method of bulk volume determination by sand displacement. This adds considerably to the precision of the values obtained on badly distorted brick. However, the method of direct measurement gives sufficiently accurate bulk volumes for all but the most irregularly shaped pieces.

In order to overcome the disadvantages in operation and expense of a vacuum pump and at the same time employ the advantages inherent in metallic containers, the apparatus shown in Fig. 3 was designed to operate on the general principle of gas expansion without employing a pump.

Apparatus The sample container is made of $\frac{1}{4}$-inch rolled steel plate with inside dimensions slightly larger than the standard dimensions of refractory brick. A cover plate made of steel plate is clamped in place by means of eight wing nut bolts and made air tight by a soft rubber gasket. However, the sample container covers could be ground to fit and made air tight by means of heavy stop-cock grease. Although a glass leveling bulb is used on the apparatus herein pictured, a metal leveling bulb could be used quite advantageously. The expansion bulb, manometer, and connections are made of glass. As these are fixed permanently and in no danger of being broken, glass is at no disadvantage. An ordinary heavy-walled rubber tube is used to connect the leveling bulb to the manometer.

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[1] G. A. Bole and F. G. Jackson, "A Simple Control Porosimeter," *Brick and Clay Rec.*, **61** [5], 314 (1922).

[2] E. E. Pressler, "A Simple Brick Porosimeter," *Jour. Amer. Ceram. Soc.*, **7**, 154 (1924).

[3] M. L. Hartmann, O. B. Westmont, and S. F. Morgan, "The Determination of the Bulk and Pore Volumes of Refractory Materials," *Jour. Amer. Ceram. Soc.*, 9 [5], 298–310 (1926).

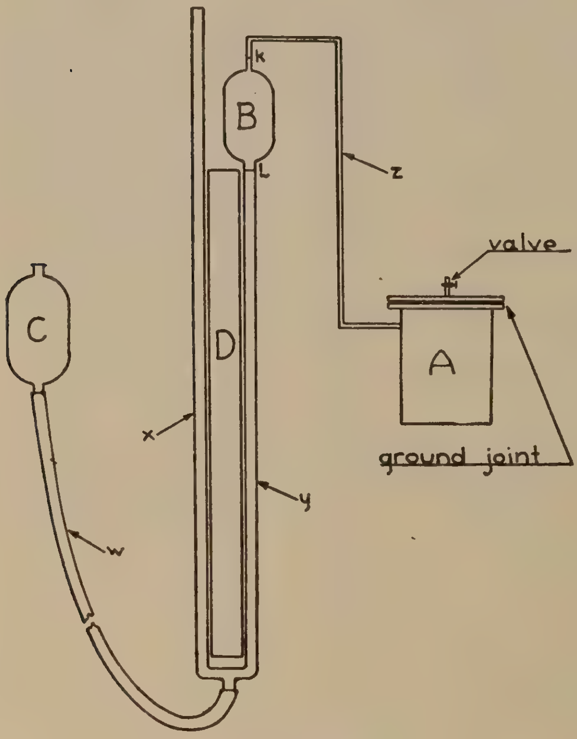

FIG. 3.

Figure 3 is a diagrammatic sketch of this apparatus. *A* is the brick container of about 2000 cc volume. The expansion bulb *B*, is made of glass and has a capacity of about 250 cc. *C* is a leveling bulb. *D* is an ordinary meter stick. The manometer, *x* and *y*, is made of glass tubing of about 5 millimeters internal diameter. Ordinary heavy-walled rubber tubing, *w*, is used and is not reinforced by a metallic covering as explained in the case of the other apparatus. *A* is connected to *B* by means of the capillary glass tube, *z*.

Operation Sufficient mercury having been previously placed in the leveling bulb to fill *B* up to the mark, *K*, the brick is placed in the sample container, *A*, and the cover put in place.

(1) *C* is elevated until the mercury level in *B* stands at *K* after which the stop-cock is closed.

(2) *C* is now lowered until the mercury level stands at *L*.

(3) The pressure difference in *x* and *y* is read on *D*. From this pressure difference the solid volume of the brick is calculated.

Calculation of Solid Volume (1) The reading, *R*, of *D* (as determined under 3 above) is subtracted from the barometric pressure in order to obtain the pressure, *p*, after the expansion process described under 1 and 2 above.

(2) Air space a, in $A = \frac{p \times B}{R}$

B is the volume from K to L

(3) Solid volume, s, of test piece $= A - a$
A is the volume of the sample container

(4) $$\text{Porosity in per cent} = \frac{v - s}{v} \times 100$$

The bulk volume, v, of the brick is determined by direct measurement with a meter stick, the average of several readings in each dimension being taken.

If apparent specific gravity is desired, it is determined by dividing the solid volume into the dry weight, w, of the brick.

Accuracy The accuracy attainable with this apparatus and method is well within the limits ordinarily required in routine factory control, research and development work. In order to compare the values obtained by this apparatus with those obtained by the apparatus described by Pressler,[1] a series of determinations were run on the same test pieces using both apparatuses. Table II shows the data obtained. For a comparison of the porosity of different types of brick as determined by the liquid absorption and the air expansion methods, see the article by Hartmann, Westmont, and Morgan[1] and the one by Pressler.[2]

TABLE II

POROSITY OF BRICK

Pressler Method	MacGee Method
43.2	42.6
37.0	37.6
34.8	35.6
28.3	28.3
15.3	15.3

Advantages This apparatus combines the advantages of the accuracy of the air-expansion method with the cheapness of the liquid absorption method. There is no operating expense, such as is inherent in the type of apparatus employing a vacuum pump, either motor driven or employing water. The leveling bulb as well as the sample container is made of metal and the apparatus is therefore of quite rugged construction. The first cost is reduced to the absolute minimum and there is no dependence upon a source of electricity or water. (Owing to the large bore of the manometer tubing, tapping is not necessary.) Working very leisurely, the porosity and apparent specific gravity of a brick can be known within fifteen minutes from the time the test is begun.

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[1] *Loc. cit.*

[2] E. E. Pressler, "Comparative Tests of Porosity and Specific Gravity on Different Types of Refractory Brick," *Jour. Amer. Ceram. Soc.*, 7 [6], 447–51 (1924).

General

It is not essential that mercury be used as the suction medium in the brick porosimeter. This is because the liquid does not come into contact with the brick. Benzyl benzoate could quite advantageously be used if proper correction is made in the pressure difference reading for the difference in its specific gravity and that of mercury. This would lower the cost of the apparatus still more and would overcome the objection to mercury on account of its weight.

Although a knowledge of the barometric pressure is essential for the calculations, a barometer is not required because the barometric pressure can be determined with either of the three pieces of apparatus. This is determined by measuring the difference in pressure obtained when the air in the empty sample container is expanded a definite amount, namely, that of the expansion chamber. The barometric pressure is calculated as follows:

$P \times V = (P - d) \times v$ in which
P = barometric pressure
d = pressure difference after V is expanded to v
V = volume of sample container
$v = V +$ volume of expansion chamber

A number of containers in various sizes and shapes could be connected by means of capillary tubing to the one expansion chamber, thus having containers designed to accommodate brick, tile, grinding wheels, etc. This is desirable where various shapes are to be tested because maximum precision is attained when the free air space around the test piece is reduced to a minimum.

The author is grateful to E. E. Pressler of the Bureau of Standards for suggesting the logical extended application of the porosimeter in the determination of true specific gravity. This can be determined on dry powdered material by enclosing it in a porous cup and determining the solid volume of the cup alone and when filled with the powder.

Conclusions

1. A direct reading porosimeter based upon the principle of gas expansion is described. This reduces the calculations required to a minimum.

2. A convenient indirect reading porosimeter which gives very accurate values for porosity and apparent specific gravity on a wide range in size and shape of test pieces is described.

3. A ruggedly constructed brick porosimeter based upon the gas expansion principle is described. This apparatus reduces the cost of this type of porosimeter below that of any thus far developed.

Bureau of Mines
Columbus, Ohio

ON THE DETERMINATION OF THE CONSTITUTION OF GLASSES[1]

By Kozo Tabata[2]

ABSTRACT

This method of determination of the constituents of glasses is entirely new in its way. It is derived from the author's experiments on the causes of the surface devitrification of glasses.

It is quite natural to produce crystals in glasses when heated several times at high temperatures. The glasses are supercooled liquids and are very viscous at low temperatures. But, when they are heated at higher temperatures, they attain low viscosities to produce crystals in them. In general, the chemical composition of the crystals produced (primary phase) in ordinary glasses without B_2O_3 is SiO_2. And for production of an elementary body of crystals of silica, there should be at least three neighboring molecules of silica moving within some ranges of speed. The motion of such molecules in glasses is set by two causes: the one is that quantity of energy given to the molecules by heating, and the other is that lowering of viscosity of the medium by heating. Heating glasses to certain temperatures is the exclusive cause of the crystal production of glasses.

This has been already explained by many persons and no ambiguity has been left unsolved.

The author has given another important cause for crystal production on glass surfaces and has described the interpretation.[3]

From these views, the author has arbitrarily defined devitrification in five degrees. They are seen in accompanying photographs. It has been determined that these degrees of devitrification were entirely coincident with the quantities of dissolved silica in glasses.

The experiments have been conducted for a series of glasses of alkali silicates and alkali lead silicates.

From the results of these experiments, the author has determined the constitutions of those silicates in glasses to be meta-disilicates and the double compounds to consist of those meta-disilicates.

As the result of the determination of the constituents of alkali silicates and of alkali lead silicate glasses, it is pointed out that the compositions of crucibles to melt glasses of different silica content, should be either rich Al_2O_3 or rich SiO_2 according to the dissolving power of glasses for silica.

Introductory

In the second report on the same subject,[3] the author has described some results on the devitrification of alkali lead silicates, giving his

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[1] Received August 11, 1926.

[2] Research Chemist in the Electrotechnical Laboratory, Ministry of Communications, Tokyo, Japan.

[3] Researches of the Electrotechnical Laboratory, No. 165, April, 1926. Tokyo, Japan.

view on the remarkable influence exerted by the presence of potassium oxide on the modes of devitrification of those glassy masses. We see also, in the photographs of the second report, that the modes of devitrification differ considerably between the cicatrized or sharp-edged portions and the flat or less sharp-edged portions. In other words, we see that the more the parts undergo surface contraction during the heat treatments the more the crystals are produced at those parts. And also the more the surfaces of the masses undergo surface contraction as a whole, the more the crystals are produced all over the surface; that is, as the differences of surface conditions both before and after the heat treatments are greater, so a greater number of crystals are produced.

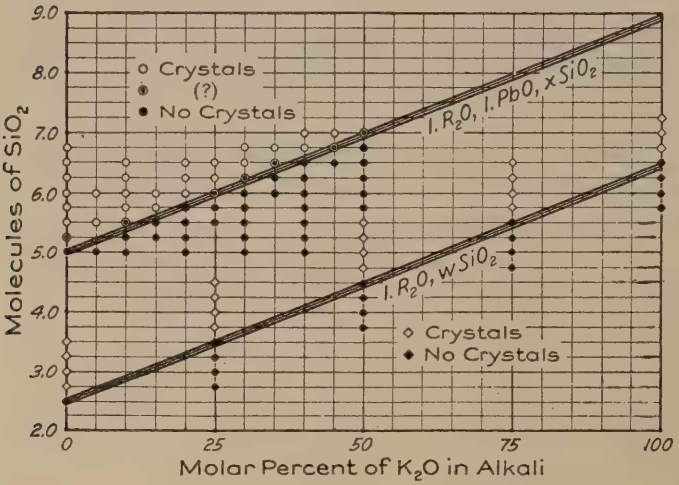

FIG. 1.—Experiments on the devitrification of alkali silicates and alkali lead silicates.

Taking account of the differences in the modes of devitrification as influenced by the surface conditions of the test samples, the author made experiments on the remarkable influence of the presence of K_2O in alkali lead silicates and in alkali silicates on the modes of devitrification after appropriate heat treatments.

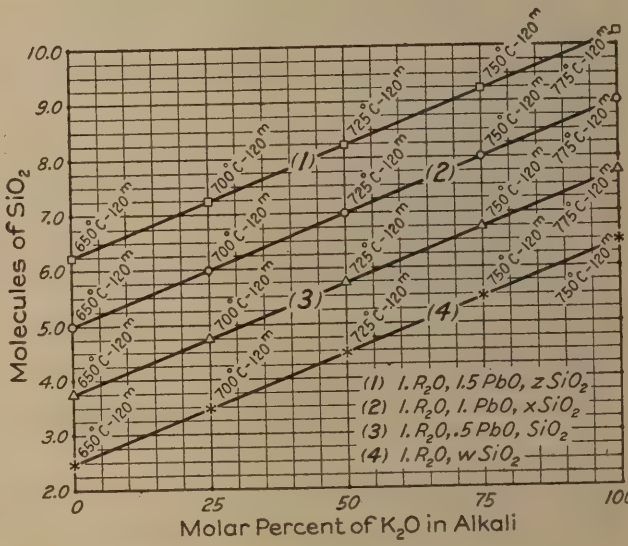

FIG. 2.—Heating conditions of devitrification along assumed lines of devitrification.

The samples used in the experiments were taken from their respective melts. Each component of the batches was dried and kept in a glass vessel avoiding moisture absorptions, etc. They were accurately weighed with a chemical balance. The chemical analysis of each material resulted as follows:

Results of Chemical Analysis

1. Sodium carbonate	99.99%
2. Potassium carbonate	99.99%
3. Silica	

	Per cent		Per cent
SiO_2	96.96	CaO	0.18
Fe_2O_3	0.074	TiO_2	0.044
Al_2O_3	2.75	MnO	0.0012
		Total	100.01

4 and 5.

		Red Lead	Litharge
Impurities	Bi_2O_3	0.00087%	0.0005%
	MnO	0.0002%	0.0002%
	ZnO	0.011	0.027
	Fe_2O_3	0.029	0.019
	Al_2O_3	0.031	0.008
	TiO_2	0.001	0.0001
	SiO_2	0.066	0.015
	Moisture	—	0.030
	Pb_3O_4 (calculated)	100.20	—
	PbO (calculated)	—	99.97

The SiO_2 powder was used as 97% purity.

The crucibles were made of 70 parts of aluminous fireclay grog and 30 parts of bond clay. Their chemical composition was about 60% Al_2O_3 and 40% SiO_2.

The melting was conducted in a gas furnace. The time of heating and melting was 8 to 12 hours. The highest temperatures were between 1400 and 1550°C. The weight of batches was about 200 grams in each case.

The well-melted glasses were air quenched, the crucibles being taken from the furnace while bright red. The dark red color of the melts disappeared in about 15 to 20 minutes.

Samples were taken generally from the central parts of the melts, and in some cases from the parts near to the walls of the crucibles. The experiments were conducted as follows.

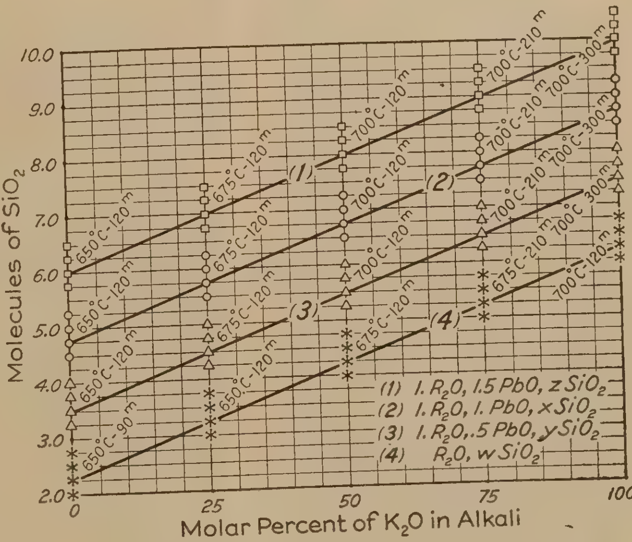

FIG. 3.—After-heating conditions for glasses along boundary lines.

In Part I, the relations between the quantities of K_2O and SiO_2 contained in series of alkali silicates composed of $x Na_2O$, $y K_2O$, $z SiO_2$, where $x+y=1$ and $z=2.5$ to 7 and the modes of devitrification upon appropriate heat treatments are described.

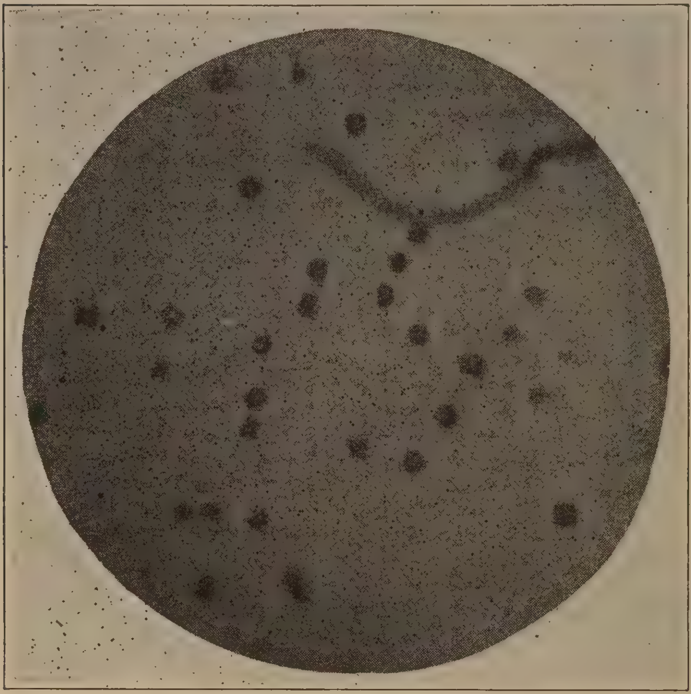

FIG. 4.—× 1000. 600°C–60m.

Those alkali silicates whose z are below 2.5 have been set outside of this experiment. They are not in direct relation to flint glasses. Their very instability in the atmosphere and probable difference of crystal forms in the primary phases from those of z of above 2.5 caused the author to make a special study of them as a separate problem.

In Part II, the effects of relative quantities of K_2O and SiO_2 on the modes of devitrification of alkali-lead-silicate melts whose batch composition is 1 R_2O, 1 PbO, $x SiO_2$, where x ranges from 4.75 to 9.5, and the results are described.

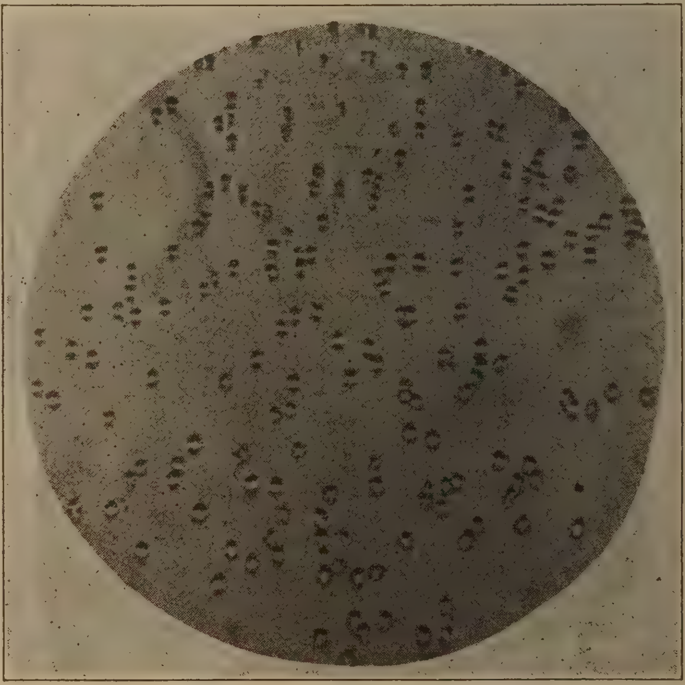

FIG. 5.—× 400. 600°C–120m.

In Part III, the degrees of devitrification as arbitrarily defined by the author are described, and the relation between the silica content and the degrees of devitrification are drawn in Figs. 19 and 20. Some photographs are attached to show the degrees of devitrification, the effects of different heat treatments on

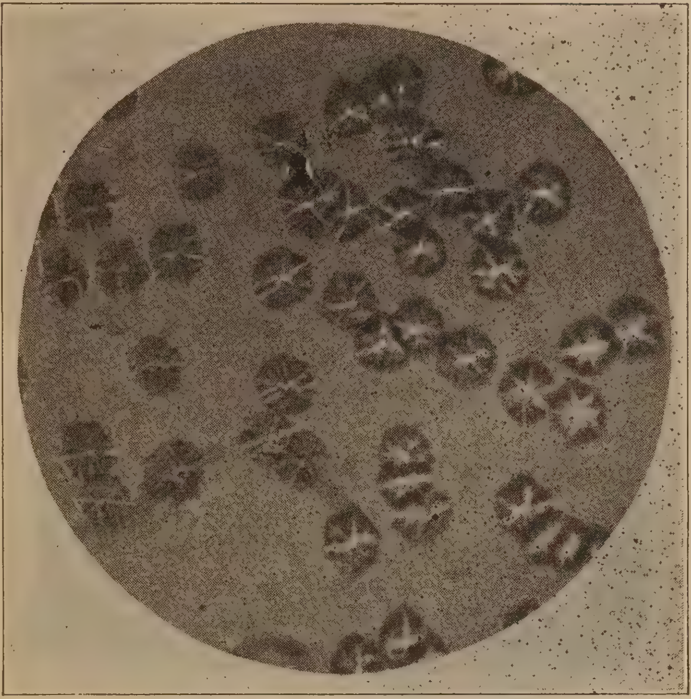

FIG. 6.—× 400. 600°C–240^m.

crystal forms, and also the linear speed of crystal growths of β-quartz.

In Part IV, the experiments which have been conducted on glasses which are situated along assumed boundary lines of devitrification for each series of 1 R_2O, 1 PbO, $x SiO_2$; 2 R_2O, 1 PbO, $y SiO_2$; and 1 R_2O, 1.5 PbO, $z SiO_2$ glasses are described. In these experiments all the samples were previously heated above 950°C, air quenched, and cicatrized before heating for devitrifying. In other words, these experiments have been conducted under conditions of the severer devitrification.

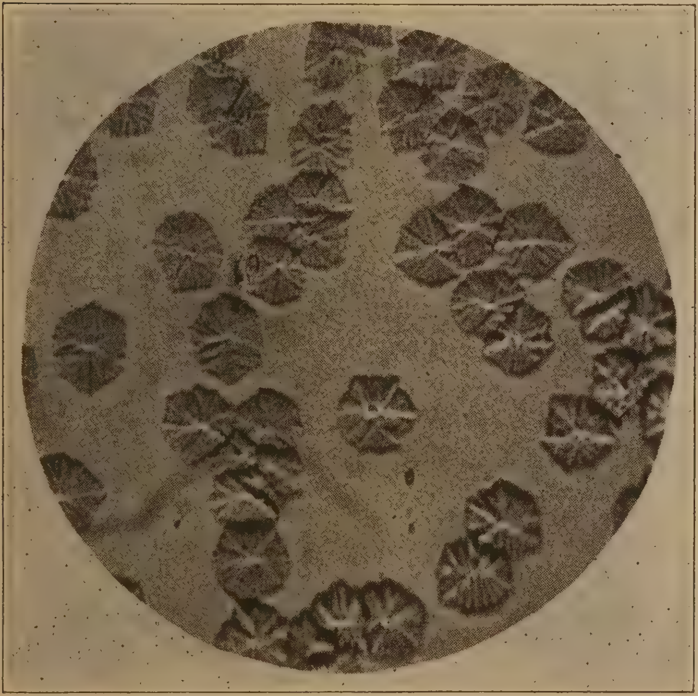

FIG. 7.—× 400. 600°C–300^m.

In Part V,[1] the corresponding experiments on glasses of 1 R_2O, 0.5 CaO, $x SiO_2$ and 1 R_2O, 1 CaO, $y SiO_2$ are described.

In Part VI,[1] conclusions are given of alkali silicates, of alkali-lead silicates, and of the suitable compositions for the crucibles.

The experiments have been done in Dai-Gobu of the Electrotechnical Laboratory, Ministry of Communications, Japan. The author would express his sincere thanks to Y. Ogawa, chief of Dai-Gobu for his thoughtful advice, and to Sukezug Kimura for his kind advice in the consideration of the results of the experiments.

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[1] Parts V and VI will appear in a paper by K. Tabata, "On the Causes of Surface Devitrification of Glasses," in *Jour. Amer. Ceram. Soc.*, January, 1927.

The author gives thanks also to his co-workers K. Yegami, S Moriyasu, Y. Toda, Z. Ishibashi, C. Oginosho, C. Ogiso for their assistance in the completion of the experiments.

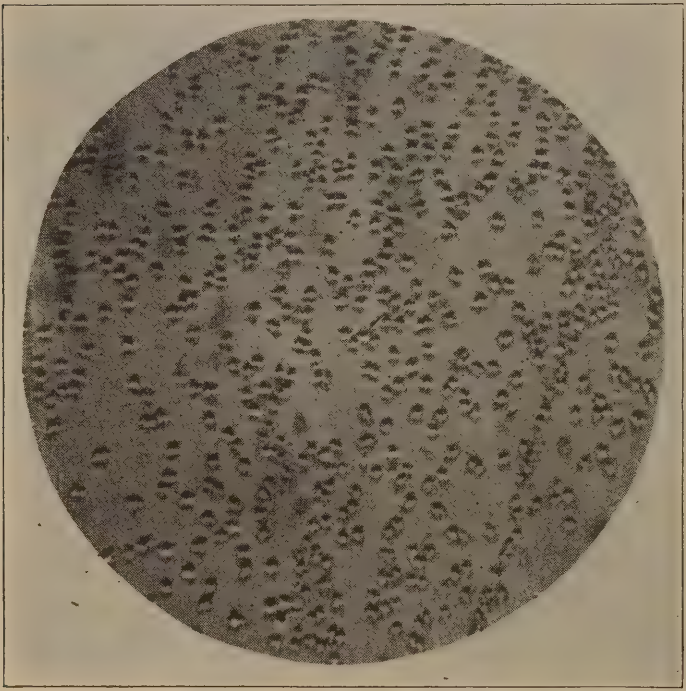

FIG. 8.—× 400. 675°C–30m.

Part I. Experiments on the Devitrification of Alkali Silicates

General Procedures Each sample of alkali silicate taken from broken pieces of air-quenched melts was cleansed and cicatrized.

Heating was conducted in an electric-muffle furnace as described in the second report.[1] Heat-treated samples were taken out from the furnace after predetermined times of heating, and air quenched.

They were pasted on glass plates and were observed through the microscope with magnifications from 90 to 1000.

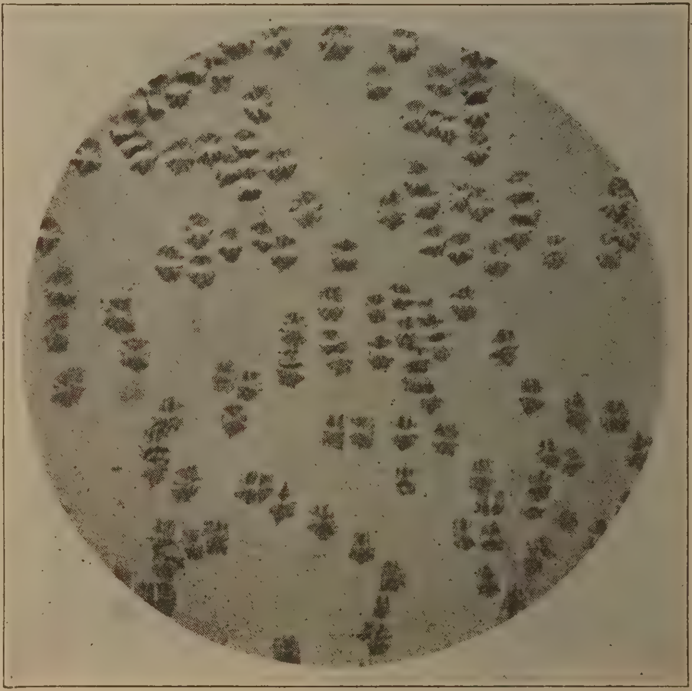

FIG. 9.—× 400. 675°C–60m.

Experiments Chemical compositions of the samples, heating conditions, surface conditions of the samples before and after the experiment, are tabulated in the Tables I to XIV.

The results gained by the microscopic observations are briefly written in degrees of devitrification, the explanation of which is to be seen in Part III.

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[1] Researches of the Electrotechnical Laboratory, No. 165.

TABLE I

Experiments on 1.0 K$_2$O – xSiO$_2$

Expt. no.	Melt no.	No. of mol. SiO$_2$	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
113	23	3	725°C–120^{m}	Broken piece	Rounded	0
149	23	3	“ “	Broken piece cicatrized	“	
112	14	4	“ “	Broken piece	“	0
150	14	4	“ “	Broken piece cicatrized	“	
110	17	5	750°C–120^{m}	Broken piece	“	0
151	17	5	“ “	Broken piece cicatrized	“	
111	20	6	“ “	Broken piece	Nearly rounded	0
130	20	6	“ “	Broken piece cicatrized	“	
105	50	6.5	“ “	Broken piece	“	0(?)
132	50	6.5	“ “	Broken piece cicatrized	“	
157	51	6.75	750 C–150^{m}	“ “	“	1
159	52	7.0	“ “	“ “	“	2
161	53	7.25	“ “	“ “	“	3

TABLE II

Experiments on 0.75 K$_2$O, 0.25 Na$_2$O–xSiO$_2$

Expt. no.	Melt no.	No. of mol. SiO$_2$	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
115	28	3	700°C–120^{m}	Broken piece	Rounded	0
145	28	3	“ “	Broken piece cicatrized	“	
100	29	3.5	“ “	Broken piece	“	0
146	29	3.5	“ “	Broken piece cicatrized	“	
68	30	4	“ “	Broken piece	“	0
147	30	4	“ “	Broken piece cicatrized	“	
155	40	4.5	725°C–120^{m}	Broken piece	“	0
148	40	4.5	“ “	Broken piece cicatrized	“	
84	39	5	“ “	Broken piece	“	0
127	39	5	“ “	Broken piece cicatrized	“	
78	38	5.5	“ “	Broken piece	“	0(?)
140	38	5.5	“ “	Broken piece cicatrized	“	
109	37	6	750°C–120^{m}	Broken piece	“	1
129	37	6	“ “	Broken piece cicatrized	“	

Table II (*concluded*)

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
108	36	6.5	“ “	Broken piece	“	2
131	36	6.5	“ “	Broken piece cicatrized	“	
171	63	5.25	725°C–120^m	“ “	“	0
172	64	4.75	“ “	“ “	“	0
173	65	5.75	“ “	“ “	“	0(?)

Table III

Experiments on $0.5\ K_2O,\ 0.5\ Na_2O–xSiO_2$

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
51	24	3	675°C–120^m	Broken piece	Rounded	0
143	24	3	“ “	Broken piece cicatrized	“	
107	48	3.5	700°C–120^m	Broken piece	“	0
144	48	3.5	“ “	Broken piece cicatrized	“	
28	15	4	“ “	Broken piece	“	0
123	15	4	“ “	Broken piece cicatrized	“	
99	47	4.5	“ “	Broken piece	“	0
138	47	4.5	“ “	Broken piece cicatrized	“	
40	18	5	725°C–120^m	Broken piece	“	1
126	18	5	“ “	Broken piece cicatrized	“	
118	49	5.5	“ “	Broken piece	“	3
41	21	6	“ “	“ “	Nearly rounded	4
168	60	4.25	700°C–120^m	Broken piece cicatrized	Rounded	0
169	61	4.75	“ “	“ “	“	0(?)
170	62	5.25	“ “	“ “	“	2

Table IV

Experiments on $0.25K_2O,\ 0.75Na_2O–xSiO_2$

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
95	46	3	675°C–120^m	Broken piece	Rounded	0
156	46	3	“ “	Broken piece cicatrized	“	
92	43	3.5	“ “	Broken piece	“	0(?)
136	43	3.5	“ “	Broken piece cicatrized	“	
87	42	4	700°C–120^m	Broken piece	“	1–2
122	42	4	“ “	Broken piece cicatrized	“	

TABLE IV (*concluded*)

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
83	41	4.5	“ “	Broken piece	“	2
124	41	4.5	“ “	Broken piece cicatrized	“	
76	31	5	725°C–120^{m}	Broken piece	“	2–3
77	32	5.5	“ “	“ “	“	3
74	33	6	“ “	“ “	Rounded cracks	3–4
75	34	6.5	“ “	“ “	Nearly rounded cracks	4
165	57	2.75	650°C–120^{m}	Broken piece cicatrized	Rounded white film	0
166	58	3.25	675°C–120^{m}	“ “	Rounded	0
167	59	3.75	“ “	“ “	“	1

TABLE V

Experiments on $1.0Na_2O–xSiO_2$

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
119	45	3	675°C–120^{m}	Broken piece	Rounded	1–2
154	45	3	“ “	Broken piece cicatrized	“	
91	44	3.5	“ “	Broken piece	“	2
153	44	3.5	“ “	Broken piece cicatrized	“	
14	13	4	700°C–120^{m}	Broken piece	“	2–3
22	16	5	725°C–120^{m}	“ “	Rounded cracks	3
34	19	6	“ “	“ “	Nearly rounded cracks	4
162	54	2.75	650°C–120^{m}	Broken piece cicatrized	Rounded white film	1
163	55	2.50	“ “	“ “	“	0(?)
164	56	2.25	625°C–120^{m}	“ “	Thick white film	0(?)

Some Remarks on the Experiments

It is a matter for consideration that the differences of endurance for weathering of the alkali silicates should account for the modes of treatment during experiments.

Those below $Na_2O, 2SiO_2$ and $K_2O, 2.5SiO_2$ should be very quickly and carefully heat treated. $Na_2O,3SiO_2$ may be safely stored in a closed glass vessel for several months without being weathered, but on the contrary K_2O, $3SiO_2$ cannot be stored. Even K_2O, $4SiO_2$ will be weathered if left standing for several (ten) days in glass-stoppered vessels.

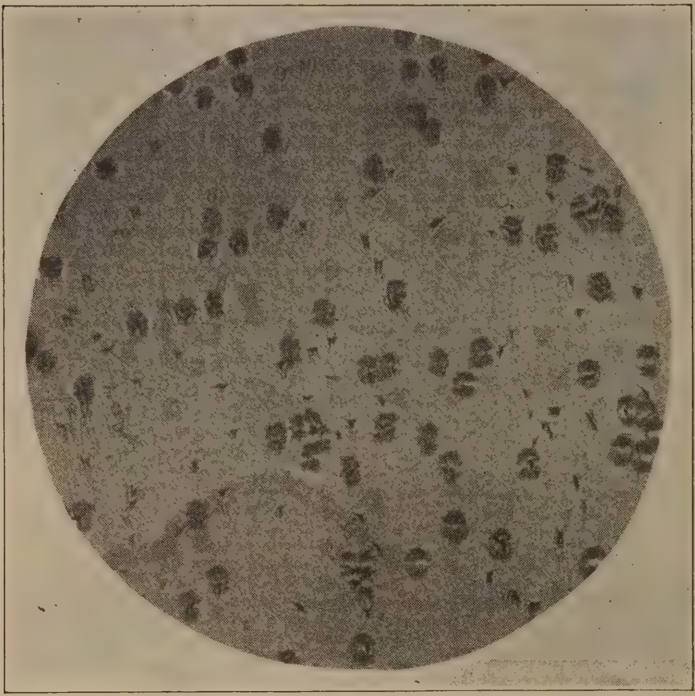

FIG. 10.—× 400. 700°C–30^m.

The author observed that during the storage of K_2O, $2SiO_2$ and Na_2O, $2SiO_2$ at ordinary temperatures, there was no crystal production of quartz under microscopic observation up to 1000 times magnification. Yet in some cases, platy crystals appeared which might be sodium metadisilicate, while standing for several days after heat treatment.

The boundary line runs on the compositions of R_2O, $2SiO_2$ plus 0.5 mols of SiO_2 for Na_2O and plus 4.5 mols of SiO_2 for K_2O, and between both end points the line elevates according to the quantities of K_2O substituted for Na_2O, and makes a straight line.

The experiments were not conducted at the sharpest conditions, so that the author gave some allowance to the widths of the line, as seen in Fig. 1.

The compounds R_2O, $2SiO_2$ seem to be more stable, which will be seen from the results after heat treatment at varying temperatures and time duration.

The author thinks the formation of R_2O, $2SiO_2$ by melting SiO_2 $+R_2O.CO_2$ is sure to combine to form alkali silicates.

Part II. Experiments on the Devitrification of Alkali Lead Silicates

General Procedure The experiments have been conducted for a series of glasses whose molar composition is $1R_2O$, $1PbO$, $xSiO_2$. Samples were taken from broken pieces of the melts which were very quickly cooled from the fluid state. Two samples of each melt, the one as it was and the other cicatrized, were put into the middle part of the electric-muffle furnace nearest to the thermocouple junction at the same time, and heated at a predetermined temperature and time duration. After the heat treatment, the samples were taken out from the furnace and air quenched. They were pasted on a separate glass plate and were observed under the microscope with magnifications of 100‘ 250, and 1,000.

They were classified by the degree of devitrification as defined by the author (see Part III).

The results were plotted as shown in Fig. 1.

Other experiments supplementary to the above have been conducted. In this case, the samples were heated previously. They flowed to a somewhat flat surface. These were air quenched and cicatrized with sharp edges of rock crystal and then again heated under conditions as described in the table.

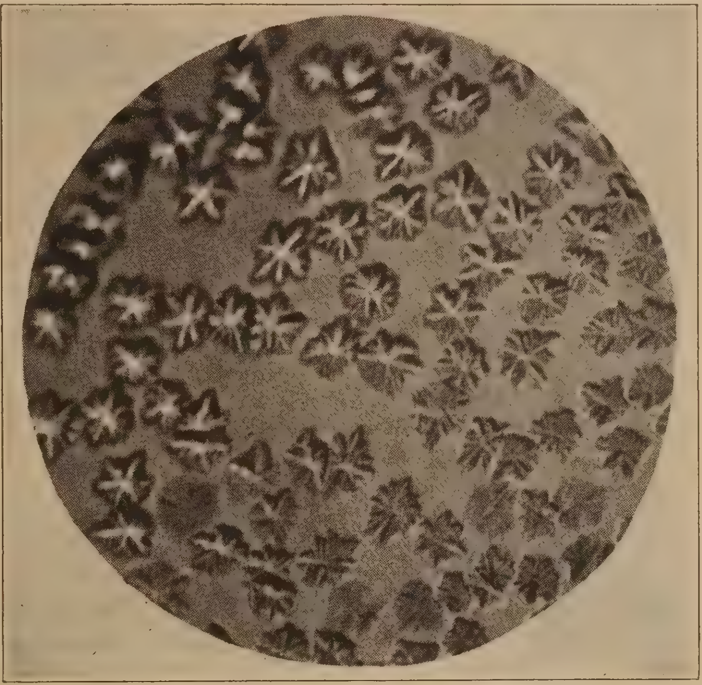

Fig. 11.—×400. 700°C–60^m.

Table VI

Experiments on $1K_2O$, $1PbO–xSiO_2$

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition Before	Surface condition After	Degree of devitrification
110	83	6.0	700°C–120^m	Broken piece cicatrized	Rounded	0
110	83	6.0	“ “	Broken piece	“	
105	78	6.5	“ “	Broken piece cicatrized	“	0
105	78	6.5	“ “	Broken piece	“	
118	92	5.5	650°C–120^m	Broken piece cicatrized	“	0
118	92	5.5	“ “	Broken piece	“	

Table VII

Experiments on $0.1K_2O$, $0.9Na_2O$–Lead Silicates

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition Before	Surface condition After	Degree of devitrification
94	69	5.0	650°C–120^m	Broken piece cicatrized	Rounded	0
94	69	“	“ “	Broken piece	“	

TABLE VII (*concluded*)

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
102	75	“	“ “	Broken piece cicatrized	“	0
102	75	“	“ “	Broken piece	“	
107	75	“	“ “	Broken piece cicatrized	“	0
107	75	“	“ “	Broken piece	“	
113	86	“	“ “	Broken piece cicatrized	“	0
113	86	“	“ “	Broken piece	“	
125	95	5.5	675°C–120^m	Broken piece cicatrized	“	0(?)
125	95	“	“ “	Broken piece	“	
98	71	6.0	700°C–120^m	Broken piece cicatrized	“	2
98	71	“	“ “	Broken piece	“	
132	105	5.25	650°C–120^m	Broken piece cicatrized	“	0
132	105	“	“ “	Broken piece	“	
139	107	5.75	675°C–120^m	Broken piece cicatrized	“	1
139	107	“	“ “	Broken piece	“	
140	107	“	“ “	Broken piece cicatrized	“	1
140	107	“	“ “	Broken piece	“	
142	101	6.5	700°C–120^m	Broken piece cicatrized	“	4
142	101	“	“ “	Broken piece	“	
147	126	5.75	675°C–120^m	Broken piece cicatrized	“	1
147	126	“	“ “	Broken piece	“	
189	152	5.0	650°C–120^m	Broken piece cicatrized	“	0
189	152	“	“ “	Broken piece	“	

TABLE VIII

Experiments on $0.2K_2O$, $0.8Na_2O$–Lead Silicates

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
101	74	5.0	650°C–120^m	Broken piece cicatrized	Rounded	0
101	74	5.0	“ “	Broken piece	“	
133	106	5.25	“ “	Broken piece cicatrized	“	0
133	106	5.25	“ “	Broken piece	“	
120	81	6.0	700°C–120^m	Broken piece cicatrized	“	0(?)
120	81	6.0	“ “	Broken piece	“	

Taple VIII (*concluded*)

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
121	88	6.0	“ “	Broken piece cicatrized	“	0(?)
121	88	6.0	“ “	Broken piece	“	
135	108	5.75	675°C–120^m	Broken piece cicatrized	“	0
135	108	5.75	“ “	Broken piece	“	
137	110	6.25	700°C–120^m	Broken piece cicatrized	“	1
137	110	6.25	“ “	Broken piece	“	
143	102	6.5	710°C–120^m	Broken piece cicatrized	“	3
143	102	6.5	“ “	Broken piece	“	
145	98	5.5	675°C–120^m	Broken piece cicatrized	“	0
145	98	5.5	“ “	Broken piece	“	
165	128	6.25	700°C–120^m	Broken piece cicatrized	Not rounded	0–1
165	128	6.25	“ “	Broken piece	“	

Table IX

Experiments on $0.3K_2O$, $0.7Na_2O$–Lead Silicates

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
96	70	5.0	650°C–120^m	Broken piece cicatrized	Rounded	0
“	“	“	“ “	Broken piece	“	
95	“	“	“ “	Broken piece cicatrized	“	0
“	“	“	“ “	Broken piece	“	
126	96	5.5	675°C–120^m	Broken piece cicatrized	“	0
“	“	“	“ “	Broken piece	“	
99	72	6.0	700°C–120^m	Broken piece cicatrized	“	0
“	“	“	“ “	Broken piece	“	
108	80	“	“ “	Broken piece cicatrized	“	0
“	“	“	“ “	Broken piece	“	
122	89	“	“ “	Broken piece cicatrized	“	0
“	“	“	“ “	Broken piece	“	
136	109	5.75	675°C–120^m	Broken piece cicatrized	“	0
“	“	“	“ “	Broken piece	“	
138	111	6.25	700°C–120^m	Broken piece cicatrized	“	0(?)
“	“	“	“ “	Broken piece	“	

Table IX (*concluded*)

Expt. no.	Melt no	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
144	103	6.5	710°C–120^{m}	Broken piece cicatrized	"	1–2
"	"	"	" "	Broken piece	"	
166	129	6.25	700°C–150^{m}	Broken piece cicatrized	"	0(?)
"	"	"	" "	Broken piece	"	
176	134	6.75	725°C–120^{m}	Broken piece cicatrized	"	2
"	"	"	" "	Broken piece	"	
191	154	5.0	650°C–120^{m}	Broken piece cicatrized	"	0
"	"	"	" "	Broken piece	"	

Table X

Experiments on $0.4K_2O$, $0.6Na_2O$–Lead Silicates

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
119	79	6.0	700°C–120^{m}	Broken piece cicatrized	Rounded	0
"	"	"	" "	Broken piece	"	
141	112	6.25	" "	Broken piece cicatrized	"	0(?)
"	"	"	" "	Broken piece	"	
149	99	5.5	675°C–120^{m}	Broken piece cicatrized	"	0
"	"	"	" "	Broken piece	"	
172	130	6.25	700°C–120^{m}	Broken piece cicatrized	"	0(?)
"	"	"	" "	Broken piece	"	
192	163	6.5	725°C–120^{m}	Broken piece cicatrized	"	0–1(?)
193	164	6.75	" "	" "	Nearly rounded	1
194	165	7.0	" "	" "	"	2

Table XI

Experiments on $0.5K_2O$, $0.5Na_2O$–Lead Silicates

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
127	97	5.5	650°C–120^{m}	Broken piece cicatrized	Rounded	0
"	"	"	" "	Broken piece	"	
111	84	6.0	700°C–120^{m}	Broken piece cicatrized	"	0
"	"	"	" "	Broken piece	"	
104	78	6.5	710°C–120^{m}	Broken piece cicatrized	"	0
"	"	"	" "	Broken piece	"	

TABLE XI (*concluded*)

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
163	162	5.5	675°C–120^{m}	Broken piece cicatrized	“	0
“	“	“	“ “	Broken piece	“	
178	136	6.75	725°C–120^{m}	Broken piece cicatrized	“	0(?)
“	“	“	“ “	Broken piece	“	
195	166	7.0	“ “	Broken piece cicatrized	Nearly rounded	0–1

TABLE XII

Experiments on $0.6K_2O$, $0.4Na_2O$–Lead Silicates

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition		Degree of devitrification
				Before	After	
150	100	5.5	650°C–120^{m}	Broken piece cicatrized	Rounded	0
“	“	“	“ “	Broken piece	“	

TABLE XIII

Supplementary Experiments on K–Na Lead Silicates

Expt. no.	No. of mols. SiO_2	Temp.-time	Previous heating	Degree of devitrification
	A. $0.05K_2O$, $0.95Na_2O$, $1PbO$, $xSiO_2$			
a	5.0	675°C–120^{m}	950°C–60^{m}	0
b	5.5	“	“	1–2
c	6.0	“	“	4
	B. $0.15K_2O$, $0.85Na_2O$, $1PbO$, $xSiO_2$			
a	5.25	675°C–120^{m}	950°C–60^{m}	0
b	5.5	“	“	0(?)
c	5.75	“	“	2
d	6.0	“	“	3
	C. $0.25K_2O$, $0.75Na_2O$, $1PbO$, $xSiO_2$			
a	5.5	700°C–120^{m}	1000°C–60^{m}	0
b	5.75	“	“	0
c	6.0	“	“	1–0
d	6.25	“	“	2
e	6.5	“	“	3
	D. $0.35K_2O$, $0.65Na_2O$, $1PbO$, $xSiO_2$			
a	6.0	725°C–120^{m}	1050°C–60^{m}	0
b	6.25	“	“	0(?)
c	6.5	“	“	0–1
d	6.75	“	“	2
	E. $0.45K_2O$, $0.55Na_2O$, $1PbO$, $xSiO_2$			
a	6.5	725°C–120^{m}	1050°C–60^{m}	0
b	6.75	“	“	0–1
c	7.0	“	“	1–2
d	7.25	“	“	3

TABLE XIV

Experiments on the Na–Lead Silicates

Expt. no.	Melt no.	No. of mol. SiO_2	Temp.-time	Surface condition Before	Surface condition After	Degree of devitrification
100	73	5.0	700°C–120^m	Broken piece cicatrized	Rounded	0(?)
"	"	"	" "	Broken piece	"	
106	"	"	650°C–120^m	Broken piece cicatrized	"	0–1
"	"	"	" "	Broken piece	"	
112	85	"	" "	Broken piece cicatrized	"	0(?)
"	"	"	" "	Broken piece	"	
109	82	6.0	700°C–120^m	Broken piece cicatrized	"	2–3
"	"	"	" "	Broken piece	"	
103	76	6.5	710°C–60^m	Broken piece cicatrized	"	4
"	"	"	" "	Broken piece	"	
117	91	5.5	675°C–120^m	Broken piece cicatrized	"	1
"	"	"	" "	Broken piece	"	
131	104	5.25	650°C–120^m	Broken piece cicatrized	"	0(?)
"	"	"	" "	Broken piece	"	
146	125	5.75	675°C–120^m	Broken piece cicatrized	"	1–2
"	"	"	" "	Broken piece	"	
148	127	"	" "	Broken piece cicatrized	"	1–2
"	"	"	" "	Broken piece	"	
173	149	6.25	700°C–120^m	Broken piece cicatrized	"	3–4
"	"	"	" "	Broken piece	"	
174	150	6.50	" "	Broken piece cicatrized	"	4
"	"	"	" "	Broken piece	"	
175	151	6.75	" "	Broken piece cicatrized	"	4
"	"	"	" "	Broken piece	"	

Summary of the Results of the Experiments

The results of the experiments are plotted in Fig. 1. Although the surface conditions were somewhat irregular and the samples were not good in a strict sense because the weighing and mixing of batch compositions were not perfect and also because the melting conditions and the conditions for crucibles did not coincide in every case, the experiments had not been done for the series of 0.75 K_2O, 0.25 Na_2O, 1PbO, xSiO; nor for those $1K_2O$, 1PbO, $xSiO_2$ near the boundary line.

It seemed to be somewhat hazardous to draw a boundary line of devitrification for the series of glasses of $1R_2O$, 1PbO, $xSiO_2$ from the results of one-half the length of the entire line. However, the results of each series of glasses parallel to the ordinate in Fig. 1, resulted in distinct degrees of devitrification above the zero degree.

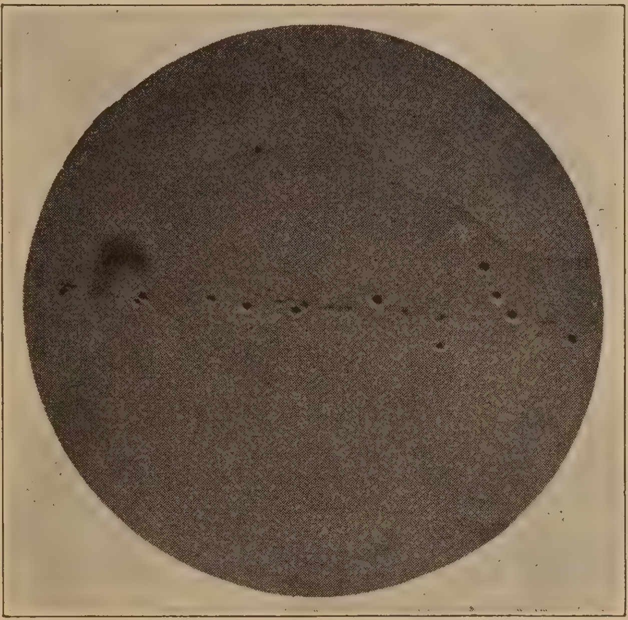

FIG. 12.—× 200. Degree 1.

It was necessary for the determination of the zero degree and one degree of any sample that skilful observations be made of definite surface conditions, appropriate heating conditions, etc.; yet for degree two, degree three, and degree four the conditions were not so strict. In other words the vigorous crystal production of those glasses overcame the minute differences in the conditions and rather regular devitrification on the surface had resulted. Degrees proceeded by one with the increase of 0.25 mols of silica for a series of glasses parallel to the ordinate.

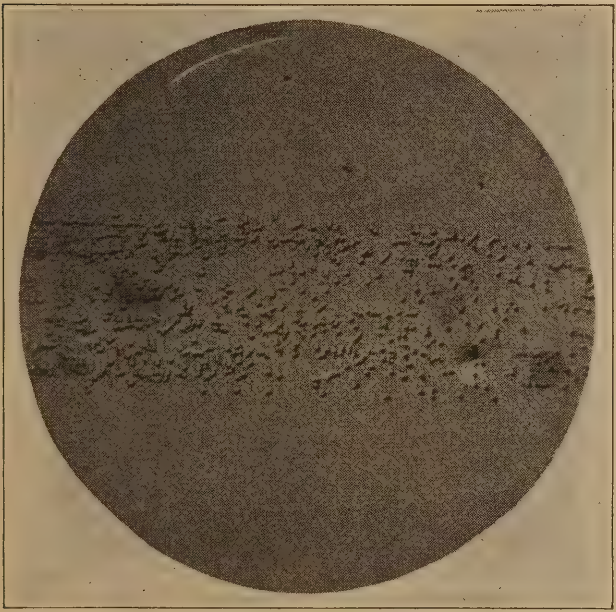

FIG. 13.—× 200. Degree 2.

The state of crystal production had been cautiously observed with considerations of different heating conditions. Observations on these points gave something to the author. The degrees moved sometimes by half under different heating temperatures.

Thus, the author drew an assumed boundary line of devitrification for the series of glasses, 1 R_2O, 1 PbO, $xSiO_2$.

The corresponding boundary lines of 1 R_2O, $wSiO_2$, and of 1 R_2O, 1 PbO, $xSiO_2$ ran parallel to each other.

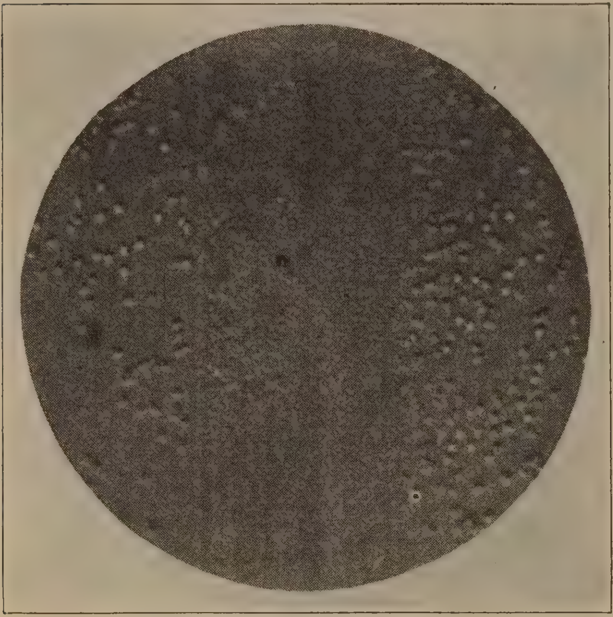

FIG. 14.—× 200. Degree 3.

Part III. Degrees of Devitrification

Classification of Degree of Devitrification

The author classified the degrees of devitrification as follows:

Degree 0, no crystals;

Degree 1, a few, minute crystals at specified places such as at sharpest edges of cicatrices.

Degree 2, many crystals along sharp edges or at cicatrized portion.

Degree 3, crystals on all the surfaces, namely, crystals produced on the glass surfaces without sharp edges or cicatrices.

Degree 4, crystals cover all over the surfaces or maximum production of crystals on the surfaces.

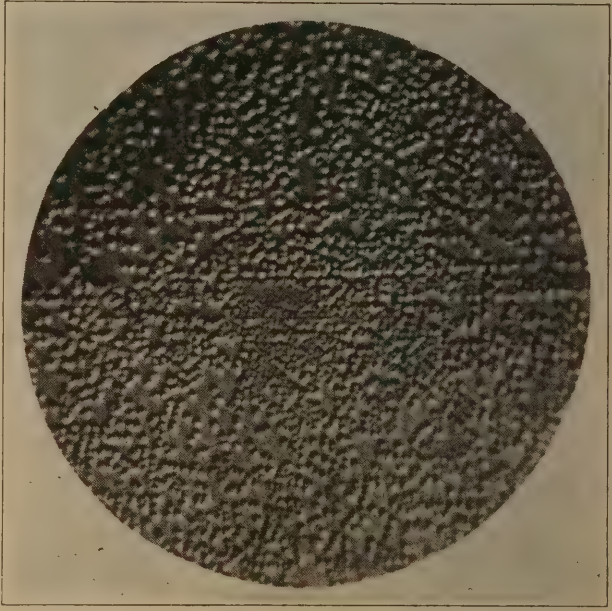

FIG. 15.—× 200. Degree 4.

This classification is very convenient in comparing the results of experiments on devitrification of similar kinds of glasses having different percentage compositions.

The basis of this classification depends on the author's view of the causes of surface devitrification of glasses.[1] The formation of crystal nuclei or crystal centers is mainly effected by the heating temperatures. Owing to the greater viscosity of glasses containing high percentages of SiO_2 molecules, some glasses which are situated along or above boundary lines of devitrification, are difficult to soften in 120 minutes heating at temperatures below 700°C.

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[1] To appear in *Jour. Amer. Ceram. Soc.*, January, 1927.

The author has assigned the minimum time of heating at 120 minutes and the temperature of heating is such that, after the heat treatments, the samples become round by surface contraction.

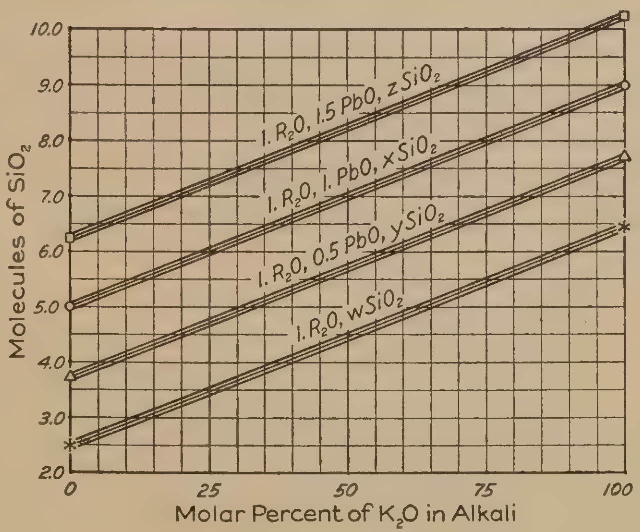

FIG. 16.—Assumed boundary lines of devitrification for alkali silicates and alkali lead silicates.

However, the most important thing in the manipulation is that the sharpest edges round up very slowly or only surface contraction takes place which is caused by surface tension acting to deform the sharp edges. In other words, the flow of glasses at sharp edges caused by other than surface contraction should be avoided, or any disturbance in crystal nucleus formation during heat treatments should be avoided. It is very desirable to use temperatures between 650–675° or 625–700°C for devitrification, as in these ranges of temperature, the crystals to be produced are definite (being β-quartz), and the linear rates of growth of β-quartz are greater than other types of crystals. Photographs show the rates of linear growth of β-quartz and those of tridymite (?). The samples were Marconi M. T. 4 glass, and no cicatrices. The experiments were conducted at an early period of the author's experiments when the surface conditions had not been so seriously considered. The magnifications were 400 times except one, that of 600°C – 120^m.

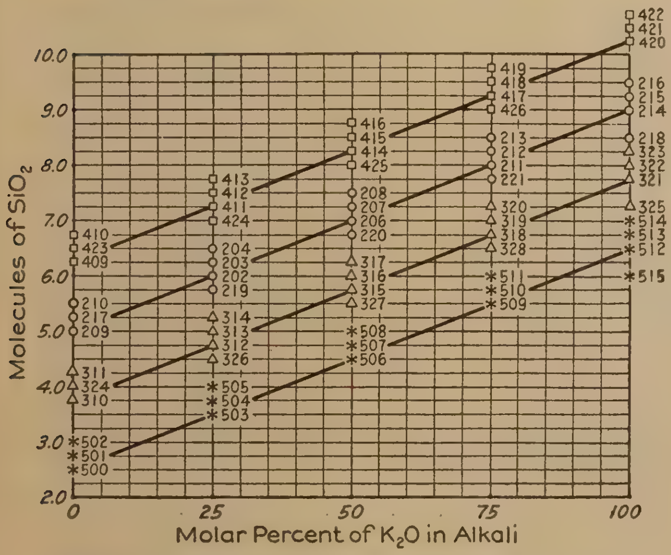

FIG. 17.—Melt numbers and experiment numbers along assumed lines of devitrification.

To observe the crystals produced, it is necessary that the crystals have some size.

When the glasses for experiment are previously heated and quenched from about 900°C or above, and the heating for crystal center formation is above 725°C or more, different modifications of SiO_2 crystals other than β-quartz are occasionally produced which have a different rate of linear speed of crystal growths.[1]

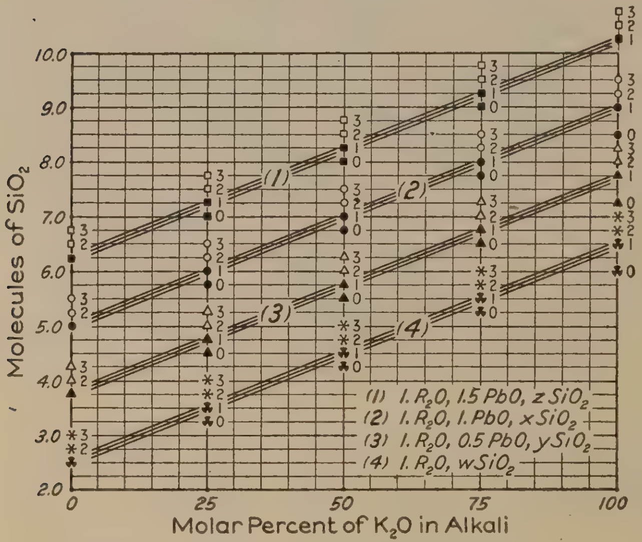

FIG. 18.—Degrees of devitrification along assumed lines of devitrification. (The numbers show degrees of devitrification.)

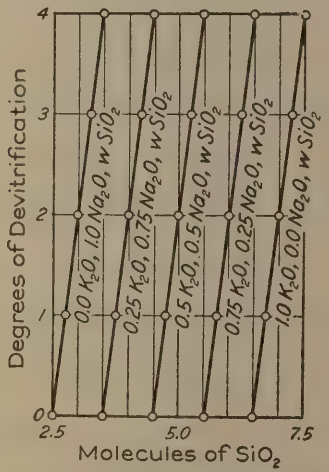

FIG. 19.—Degrees of devitrification for alkali lead silicates, as determined by the experiments.

For clearer observation of such crystals or those very minute crystals which did not grow to sufficient size, the author gave "after-heating conditions" for each series of glasses, as shown in Fig. 3.

Under these conditions, the crystallizations were vigorous and the growths of crystals proceeded regularly.

Part IV. Experiments Along Assumed Boundary Lines of Devitrification

From the results of the experiments on alkali silicates and on alkali lead silicates which are given in the preceding pages, the author deduced assumed lines of devitrification for alkali lead silicates, $1R_2O$, 0.5 PbO, $ySiO_2$; $1R_2O$, 1.5 PbO, $zSiO_2$ running parallel to those lines of $1R_2O$, $wSiO_2$ and $1R_2O$, 1PbO, $xSiO_2$ as are shown in Fig. 16.

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[1] The heating conditions are assigned as are seen in the Tables XV, XVI, XVII, and XVIII, for the respective series of glasses of alkali silicates and alkali lead silicates. When the compositions of glasses situated between those described, the heating conditions are set to the intermediate. And if the composition is near to some one of the assigned, the same heating conditions are given, etc.

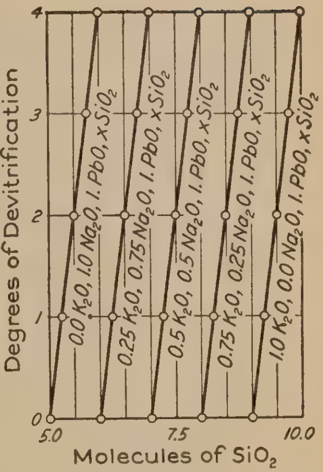

FIG. 20.—Degrees of devitrification for alkali lead silicates as determined by the experiments.

Referring to the literature upon alkali silicates and on lead silicates, the author thought it reasonable to assume only the presence of di-compounds of alkali silicates and lead silicates in glasses having such compositions under the experiments and being melted at high temperatures and being air quenched from the fluid state.

The predetermined boundary line of $1R_2O$, $1PbO$, $xSiO_2$ starts at 5 mols of silica and ends at 9 mols while that of $1R_2O$, $wSiO_2$ starts at 2.5 mols of silica and ends at 6.5 mols of silica in Fig. 1. In other words, one mol of Na_2O, $2SiO_2$ dissolves 0.5 mol of silica and one mol of K_2O, $2SiO_2$ 4.5 mols of silica. The number of mols of silica at the starting point should consist of 2.5 mols of silica for alkali silicate plus 2.5 mols of silica for lead silicate. So that 1 mol of $1PbO$, $2SiO_2$ dissolves 0.5 mols of silica without crystal production after heat treatment under the conditions of these experiments.

Thus, the author drew lines as assumed boundary lines of devitrification for $1R_2O$, $0.5\ PbO$, $ySiO_2$ and $1R_2O$, $1.5PbO$, $zSiO_2$ running parallel to those predetermined boundary lines of devitrification of $1\ R_2O$, $1\ PbO$, $xSiO_2$ and $1\ R_2O$, $wSiO_2$. The distances along the ordinate between those lines have been fixed as 1.25 mols of silica for every 0.5 mols of PbO. These are shown in Fig. 16.

General Remarks of the Experiments

In the experiments, the crucibles, the melting procedures, the rapid cooling of the melts, the weighing of the batch compositions, and heating conditions, and observations by microscope etc., had been so controlled that the results gained had been observed with the least ambiguity. However, some disturbances had occurred to those near the zero degree of devitrification for glasses of $1Na_2O$, $1PbO$, $xSiO_2$. They might be due to the insufficient dryness in the heating furnace. In some instances, the author had observed the escaping of water vapor when the door of the furnace had been opened after heat treatment.

The crucibles used in these experiments had been manufactured by the co-workers of the author. To 70 to 80 parts of aluminous grog, 30 to 20 parts of aluminous bond clay were added, well mixed and formed by skilful hand, and carefully dried and ignited at about 1200°C. They were very resistant to sudden changes of temperature. They were safely heated with batch of about 200 grams in them to about 1000°C or higher in a few minutes; and also could be cooled to some 500°C in the air with melts in the fluid state.

For batch mixtures, elutriated silica powder of 97% purity with 2.75% Al_2O_3 and a few impurities, and chemically pure anhydrous Na_2CO_3, K_2CO_3, PbO, and Pb_3O_4 were used.

Each was perfectly dried and preserved in separate glass vessels. Each was accurately weighed with a chemical balance.

They were well mixed in porcelain mortars and transferred into crucibles.

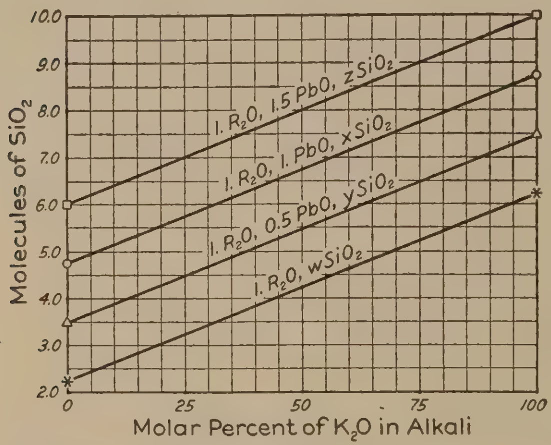

FIG. 21.—Results of experiments. The boundary lines.

Three crucibles had been heated at the same time in a gas furnace. The heating temperatures had been quickly raised to about 800°C and then slowly to about 1100°C. After the end of sintering of the entire mass, the temperatures had been quickly elevated again to about 1400 to 1550°C according to the silica content of the batch. The highest temperatures had been continued from two to six hours according to the silica content of the glasses melted.

The cooling of the melts was always done quickly. The fire of the furnace was put out, the door was opened, and the crucibles were taken up with the tongs into the atmosphere while they were at white heat. The color of the melts became dark red in several minutes.

The cooled melts were broken to pieces; the pieces from the central parts were used as the samples for the experiments of devitrification.

The samples were heated previously above 950 or 1000°C for about 60 minutes in an electric-muffle furnace. The curvatures of the flowed mass were somewhat different according to their chemical composition. Yet, it might generally be said that the surface conditions had been improved very much compared with those conditions as used in the experiments in Parts I and II. These flowed pieces of test samples were quenched in the air and cicatrized with sharp edges of rock crystals.

In devitrifying those samples, the heating was conducted under the conditions as assigned (see Part III) and the microscopic observations were the same as before.

In the course of the experiments, close attention was paid to the samples in their size, form, cicatrization, and other points which might affect the surface contraction. In the microscopic observations not only the number, size, and form of crystals produced were carefully observed but also the changes of surface curvatures, and state of bubbles appearing during heating, etc., were cautiously taken into account for the degrees of devitrification.

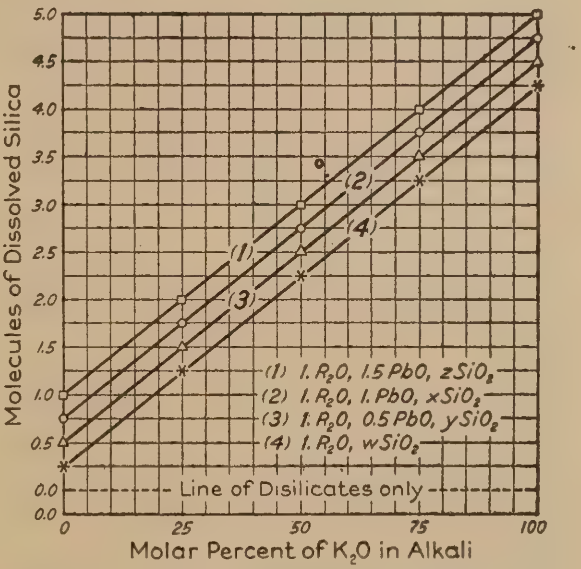

FIG. 22.—Saturation lines for alkali lead silicates and for alkali silicates.

The Experiments The chemical compositions (batch) of the sample glasses, the melt numbers, the experiment numbers, heating conditions, surface conditions, and degrees of devitrification are tabulated in Tables XV to XVIII. In the tables, heating conditions, *a* denotes heating for flowing samples to get unique curvature and *b* expresses conditions of heating for devitrification.

TABLE XV

Experiments on $1R_2O$, $0.5PbO$, $ySiO_2$

Melt nos. Expt. nos.	No. of mols. K_2O	Na_2O	SiO_2	Heating conditions *a*	*b*	Surface conditions Before	After	Degree of devitrification
310	0.0	1.0	3.75	950°C–60^{m}	650°C–120^{m}	Flat-round	Spheric-round	1
324	"	"	4.0	" "	" "	"	"	2
311	"	"	4.25	" "	" "	"	"	3
326	0.25	0.75	4.5	1000°C–60^{m}	675°C–120^{m}	"	"	0
312	"	"	4.75	" "	" "	"	"	1
313	"	"	5.0	" "	675°C–180^{m}	"	"	2
314	"	"	5.25	" "	" "	"	"	3
327	0.5	0.5	5.5	" "	700°C–120^{m}	"	"	0
315	"	"	5.75	" "	" "	"	"	1
316	"	"	6.0	1050°C–60^{m}	700°C–150^{m}	"	"	2
317	"	"	6.25	" "	" "	"	"	3
328	0.75	0.25	6.5	" "	700°C–210^{m}	"	"	0
318	"	"	6.75	" "	" "	"	"	1
319	"	"	7.0	1100°C–60^{m}	700°C–240^{m}	"	"	2
320	"	"	7.25	" "	" "	"	"	3
321	1.0	0.0	7.75	" "	700°C–300^{m}	"	"	1
322	"	"	8.0	" "	" "	"	"	2
323	"	"	8.25	" "	" "	"	"	3
325	"	"	7.25	" "	" "	"	"	0

TABLE XVI

Experiments on $1R_2O$, 1PbO, $xSiO_2$

Melt nos.	No. of mols.			Heating conditions		Surface conditions		Degree of
Expt.nos.	K_2O	Na_2O	SiO_2	*a*	*b*	Before	After	devitrification
209	0.0	1.0	5.0	950°C–60^{m}	650°C–120^{m}	Flat-round	Spheric-round	1
217	“	“	5.25	“ “	“ “	“	“	2
210	“	“	5.5	“ “	“ “	“	“	3
219	0.25	0.75	5.75	1000°C–60^{m}	675°C–120^{m}	“	“	0
202	“	“	6.0	“ “	“ “	“	“	1
203	“	“	6.25	“ “	675°C–180^{m}	“	“	2
204	“	“	6.5	“ “	“ “	“	“	3
220	0.5	0.5	6.75	“ “	700°C–120^{m}	“	“	0
206	“	“	7.0	“ “	“ “	“	“	1
207	“	“	7.25	1050°C–60^{m}	700°C–150^{m}	“	“	2
208	“	“	7.5	“ “	“ “	“	“	3
221	0.75	0.25	7.75	“ “	700°C–210^{m}	“	“	0
211	“	“	8.0	“ “	“ “	“	“	1
212	“	“	8.25	1100°C–60^{m}	700°C–240^{m}	“	“	2
213	“	“	8.5	“ “	“ “	“	“	3
218	1.0	0.0	8.5	“ “	700°C–300^{m}	“	“	0
214	“	“	9.0	“ “	“ “	“	“	1
215	“	“	9.25	“ “	“ “	“	“	2
216	“	“	9.5	“ “	“ “	“	“	3

TABLE XVII

Experiments on $1R_2O$, 1.5PbO, $zSiO_2$

Melt nos.	No. of mols.			Heating conditions		Surface conditions		Degrees of
Expt. nos.	K_2O	Na_2O	SiO_2	*a*	*b*	Before	After	devitrification
409	0.0	1.0	6.25	950°C–60^{m}	650°C–120^{m}	Flat-round	Spheric-round	1
423	“	“	6.5	“ “	“ “	“	“	2
410	“	“	6.75	“ “	“ “	“	“	3
424	0.25	0.75	7.0	1000°C–60^{m}	675°C–120^{m}	“	“	0
411	“	“	7.25	“ “	“ “	“	“	1
412	“	“	7.5	“ “	675°C–180^{m}	“	“	2
413	“	“	7.75	“ “	“ “	“	“	3
425	0.5	0.5	8.0	“ “	700°C–120^{m}	“	“	0
414	“	“	8.25	“ “	“ “	“	“	1
415	“	“	8.5	1050°C–60^{m}	700°C–150^{m}	“	“	2
416	“	“	8.75	“ “	“ “	“	“	3
426	0.75	0.25	9.0	“ “	700°C–210^{m}	“	“	0
417	“	“	9.25	“ “	“ “	“	“	1
418	“	“	9.5	1100°C–60^{m}	700°C–240^{m}	“	“	2
419	“	“	9.75	“ “	“ “	“	“	3
420	1.0	0.0	10.25	“ “	700°C–300^{m}	“	“	1
421	“	“	10.5	“ “	“ “	“	“	2
422	“	“	10.75	“ “	“ “	“	“	3

TABLE XVIII

Experiments on $1R_2O, wSiO_2$

Melt nos.	No. of mols.			Heating conditions		Surface conditions		Degrees of
Expt. nos.	K_2O	Na_2O	SiO_2	a	b	before	after	devitrification
500	0.0	1.0	2.5	950°C–60^{m}	650°C–120^{m}	Flat-round	Spheric-round	1
501	"	"	2.75	" "	" "	"	"	2
502	"	"	3.0	" "	" "	"	"	3
503	0.25	0.75	3.5	" "	" "	"	"	1
504	"	"	3.75	" "	" "	"	"	2
505	"	"	4.0	" "	" "	"	"	3
506	0.5	0.5	4.5	" "	675°C–120^{m}	"	"	1
507	"	"	4.75	" "	" "	"	"	2
508	"	"	5.0	1000°C–60^{m}	" "	"	"	3
509	0.75	0.25	5.5	" "	" "	"	"	1
510	"	"	5.75	" "	" "	"	"	2
511	"	"	6.0	" "	700°C–120^{m}	"	"	3
515	1.0	0.0	6.0	" "	" "	"	"	0
512	"	"	6.5	" "	" "	"	"	1
513	"	"	6.75	" "	" "	"	"	2
514	"	"	7.0	" "	" "	"	"	3

During the observations, the author gave some consideration to the practical applications of this method of devitrification, and gave another heating condition for glasses along boundary lines of devitrification, as shown in Fig. 2. When the crystals are minute and the magnifying powers of the microscope are low, the observation may become somewhat troublesome. It is better to heat samples again under conditions shown in Fig. 3. By the reheating minute crystals will grow large enough to be easily observed. In Fig. 17 the experiment numbers, melt numbers, the compositions, and in Fig. 8 the degree of devitrification, respectively, are plotted for brevity.

Summary of the Results

From the results of the experiments, it is summarized that:

1. The solution of silica in alkali silicates is different according to the relative quantities of K_2O and Na_2O contained in them. One mol of $1Na_2O, 2SiO_2$ dissolves up to about 0.25 mols of SiO_2 without producing crystals of β-quartz upon heating at 650°C–120 minutes, and $1K_2O, 2SiO_2$ dissolves up to about 4.25 mols of SiO_2 with no production of SiO_2 crystals on heating at 725°C–120 minutes.

2. The quantities of silica dissolved in series of Na-K silicate glasses without crystal production on appropriate heat treatments increase by the substitution of Na by K, and the relation is entirely "additive."

3. The author names the line connecting the uppermost points of no crystal production, "boundary line of devitrification" for technical use or "saturation line" for scientific use.

4. This boundary line of alkali silicate is a straight line.

5. The line connecting points of no crystal production for each alkali

lead silicate of $1R_2O$, 0.5 PbO, $ySiO_2$; $1R_2O$, 1PbO, $xSiO_2$; and $1R_2O$, 1.5 PbO, $zSiO_2$ is also a straight line.

6. These four straight lines run parallel to each other.

7. The distances of these four lines along ordinates are equal. Starting at $1R_2O$, $wSiO_2$, the distance is 1.25 mols of silica to $1R_2O$, 0.5 PbO, $ySiO_2$, to $1R_2O$, 1PbO, $xSiO_2$ and to $1R_2O$, 1.5 PbO, $zSiO_2$ respectively as shown in Fig. 5.

8. The degree of devitrification is clearly distinguished. The degrees 0, 1, 2, 3, and 4 always follow by a difference of about 0.25 mols of SiO_2 in excess.

9. The crystals (in primary phase) produced are β-quartz under the conditions as applied at temperatures below 675°C. Some, below 650°C and under shorter time of heating, seemed to be α-quartz.

10. The crystals (in primary phase) produced above 725°C are of β-quartz and in some cases are of tridymite (?).

11. The crystals of β-quartz produced are always the top parts along *c* axis, no other planes appearing.

12. The Tables I and II are the calculated percentage compositions on degree 0 and degree 1 lines of devitrification.

13. The degrees of devitrification obtained by the experiments are plotted in Figure 18.

14. As the results of the experiments, the degree 0 lines of devitrification are drawn as shown in Fig. 9.

TABLE XIX

Chemical Compositions of Least Devitrifiable Glasses

Molar compositions on degree 1 lines	Melt nos.	Percentage compositions (calculated)				
		K_2O	Na_2O	PbO	SiO_2	Total
$R_2O, 1.5PbO, zSiO_2$	409	—	8.01	43.27	48.71	99.99
	411	2.80	5.52	39.77	51.92	100.01
	414	5.17	3.41	36.78	54.65	100.01
	417	7.22	1.58	34.21	56.99	99.99
	420	8.99	—	31.98	59.05	100.02
$1R_2O, 1.0PbO, xSiO_2$	209	—	10.57	38.05	51.40	100.02
	202	3.60	7.10	34.07	55.23	100.00
	206	6.51	4.29	30.86	58.35	100.01
	211	8.93	1.96	28.19	60.89	99.97
	214	10.94	—	25.98	63.08	100.00
$1R_2O, 0.5PbO, ySiO_2$	310	—	15.52	29.93	56.53	99.98
	312	5.03	9.94	23.84	61.19	100.00
	315	8.78	5.78	20.80	64.65	100.01
	318	11.69	2.56	18.45	67.32	100.02
	321	14.00	—	16.58	69.42	100.00
$1R_2O, wSiO_2$	500	—	29.13	—	70.86	99.99
	503	8.38	16.54	—	75.08	100.00
	506	13.48	8.87	—	77.66	100.01
	509	16.91	3.71	—	79.38	100.00
	510	19.37	—	—	80.61	99.98

TABLE XX

Chemical Compositions of Glasses on Boundary Lines

	Molar compositions on degree 0 lines			Percentage compositions (calculated)				
				K_2O	Na_2O	PbO	SiO_2	Total
$1\ R_2O$, $1.5\ PbO$, $zSiO_2$	$1Na_2O$,	$1.5PbO$,	$6SiO_2$	—	8.173	44.134	47.693	100.000
	$0.25\ K_2O$ $0.75\ Na_2O$	"	7 "	2.848	5.623	40.486	51.043	"
	$0.5\ K_2O$ $0.5\ Na_2O$	"	8 "	5.261	3.463	37.395	53.887	100.006
	$0.75\ K_2O$ $0.25Na_2O$	"	9 "	7.332	1.608	34.743	56.317	100.000
	$1K_2O$			9.128	—	32.442	58.430	"
$1\ R_2O$ $1.0\ PbO$, $xSiO_2$	$1Na_2O$,	$1.0PbO$,	$4.75SiO_2$	—	10.846	39.047	50.107	"
	$0.25K_2O$ $0.75Na_2O$	"	4.75 "	3.680	7.266	34.876	54.178	"
	$0.5K_2O$ $0.5Na_2O$	"	6.75 "	6.650	4.377	31.511	57.463	100.001
	$0.75K_2O$ $0.25Na_2O$	"	7.75 "	9.096	1.966	28.738	60.170	100.000
	$1K_2O$		18.75 "	11.148	—	26.414	62.438	"
$1\ R_2O$ $0.5\ PbO$, $ySiO_2$	$1Na_2O$,	$0.5PbO$,	$3.5SiO_2$	—	16.118	29.014	54.868	"
	$0.25K_2O$ $0.75Na_2O$	"	4.5 "	5.199	10.265	24.636	59.901	100.001
	$0.5K_2O$ $0.5Na_2O$	"	5.5 "	9.034	5.946	21.406	63.614	100.000
	$0.75K_2O$ $0.25Na_2O$	"	6.5 "	11.981	2.628	18.925	66.466	"
	$1K_2O$	"	7.5 "	14.315	—	16.959	68.726	"
$1\ R_2O$, $wSiO_2$	$1Na_2O$,		$2.25SiO_2$	—	31.365	—	68.635	"
	$0.25K_2O$ $0.75Na_2O$		3.25 "	8.853	17.480	—	73.668	"
	$0.5K_2O$ $0.5Na_2O$		4.25 "	14.086	9.271	—	76.642	99.999
	$0.75K_2O$ $0.25Na_2O$		5.25 "	17.543	3.849	—	78.608	100.000
	$1K_2O$		6.25 "	19.997	—	—	80.003	"

Conclusions

1. The constitutions of alkali silicates are xNa_2O, $2SiO_2+yK_2O$, $2SiO_2+zSiO_2$. The dissolving powers of Na_2O, $2SiO_2$ and K_2O, $2SiO_2$ for SiO_2 differ very much. The author assumes the cause of the different dissolving power to be attributed to the difference of the atomic structure of both atoms of Na and K.

2. The constitutions of ordinary flint glasses are $x(1R_2O,\ 2SiO_2,\ 1PbO,\ 2SiO_2)+y(1R_2O,\ 2SiO_2)+z(1PbO,\ 2SiO_2)+wSiO_2$.

3. For the compositions of crucibles for flint glass melting, the author gives the following standards:

(*a*) For glasses which contain excess silica or situated above saturation lines in Fig. 22: silica rich crucibles.

(*b*) For glasses which contain insufficient silica or situated below saturation lines in Fig. 22: alumina rich crucibles.

SOURCES OF ERROR IN GLASS VOLUMETRIC APPARATUS[1]

By H. V. E. M. Renn

ABSTRACT

The most serious source of error is the original calibrating operation. Errors introduced are due principally to following causes: (*a*) volumetric inaccuracy, (*b*) variation of bore, (*c*) delivery time, (*d*) incorrect marking of the meniscus, (*e*) after-working of the glass. Elimination of errors due to these causes is discussed. An apparatus for the calibration of volumetric apparatus is described. A source of error that is not usually recognized is the occurence of after-changes in the glass during a period immediately following manufacture. The length of this period varies with the composition of the glass. Experiments by the writer upon glass volumetric apparatus show that a period of seven months is usually sufficient in order to avoid excessive error from this source.

In the manufacture of glass volumetric apparatus every precaution has to be taken to avoid the introduction of error. What is regarded as the most serious source of error is the original calibrating operation, in which the required volume or some definite fraction of it, is marked off on the vessel.

Cause of Errors

Errors introduced are, in the main, due to the following causes:

(*a*) Volumetric inaccuracy
(*b*) Variation of bore
(*c*) Delivery time
(*d*) Incorrect marking of the meniscus
(*e*) After-working of the glass

(a) Volumetric Inaccuracy The most accurate means of measuring a volume of liquid is, of course, by weighing, but this is long and tedious and is not by any means a commercial proposition. Various forms of apparatus have been proposed from time to time[2] which are intended to transfer a rapidly and accurately measured volume of liquid to the vessel being calibrated. The basis of most such apparatus is volumetric measurement, consisting in drawing off the required volume of liquid from a storage bottle into an accurately calibrated measuring pipette and by means of a double-way stop-cock, transferring it to the vessel undergoing calibration. The apparatus suggested by Stott[3] (Fig. 1) for calibrating burette tubes is typically illustrative of this method. The following is a brief description of the apparatus.

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[1] Received June 30, 1926.

[2] English, *Jour. Soc. Glass Tech.*, **2**, 216, **3**, 34; Stott, *ibid.*, **8**, 38; H. V. E. M. Renn, *Ind. Chem.*, **2** [13], 55.

[3] *Loc. cit.*

A piece of thermometer tubing, *A*, is attached to the top of the burette tube by means of rubber tubing and an adapter. The thermometer tubing controls the rate at which air enters the top of the burette tube and therefore also the rate of outflow of water from the burette. No difficulty will be experienced in selecting tubing which will give a satisfactory rate of outflow. A period of outflow of about 150 seconds (the approximate mean of the limits allowed by the U. S. Bureau of Standards) would be found most suitable, and this must also be the time occupied in emptying the finished burette in practice. The other end, *B*, of the burette is drawn down to a diameter suitable for sealing on the stop-cock when the burette has been graduated and this narrowed end is connected to the apparatus. The stop-cock *C* is opened, *D* and *E* being closed, until a few milliliters of water have entered the tube. The tap, *C*, is now closed and *D* is opened in order to fill the connecting tube so that the lower part of the apparatus is free from air, and also to enable an accurate setting to be made on the lower graduation mark, *F*, of the pipette. The burette tube can now be completely filled and successive intervals of 10 milliliters drawn off into the pipette up the mark, *G*, and emptied to *F*, the same period of drainage being allowed for each interval. The capacity from *F* to *G* can be checked gravimetrically at any time so that the method allows small probability of error.

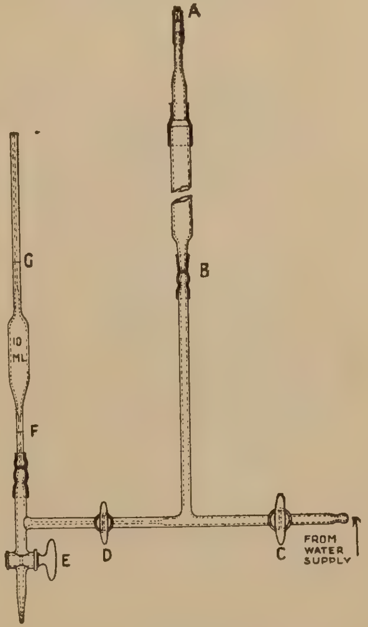

FIG. 1.

The present writer has found that, in practice, it is advisable to graduate a portion of the tube above and below the mark, *G*, so that, in the event of any change in the capacity taking place, a correction can be made by using some other point on the graduated scale. It was also found convenient to replace the two stop-cocks, *E* and *D*, by one three-way tap.

The fundamental condition fulfilled by the apparatus is the automatic control of outflow, the probability of error due to variation in the rate of drainage, being thus greatly reduced.

The present writer has used a similar apparatus for the calibration of some hundreds of burettes examined at the English National Physical Laboratory. The error limit was at that time only 0.04 cc, which was the maximum error allowed at any point tested and also the maximum difference allowed between the errors at any two points tested. This limit is slightly less than that at present allowed by the Bureau of Standards.

(b) Variation of Bore It is possible to introduce grave errors due to the selection of burette tubing of excessive variation of bore. This has been illustrated by a simple calculation.[1] A variation of only 0.2 mm in the parallelism of the bore of a 50 ml burette tube over a length of 138.2 mm (equivalent to an interval of exactly 10 ml) was shown to give rise to an error of 0.052 ml. This occurs when the method used for dividing or graduating the burette is on the basis of length. A common method of graduating a calibrated interval is to divide the distance between two adjacent calibration marks into a number of equal divisions, or spaces. If any variation exists in the parallelism of the bore, theoretically no two divisions will represent exactly the same volume. If the variation is slight, however, the error introduced will be so small as to be negligible.

In the example given above, the sectional variation was 0.2 mm, so that when the interval was graduated into 100 divisions of equal spacing, a gradual increase in volume would occur at each division from the narrow end of the tube to the wide end. As the spacing during the dividing operation is determined on the basis of the mean volume, it follows that the capacity of the divisions towards the narrow end would be less than the mean, while the capacity of those at the wide end would be greater. Thus, in testing with zero (at the narrow end) as the starting point of each interval tested, the errors of minus value that would at first occur would be eventually cancelled, and when the 10 ml mark is reached the capacity would be found correct. This can be seen by referring to the curve in Fig. 2.

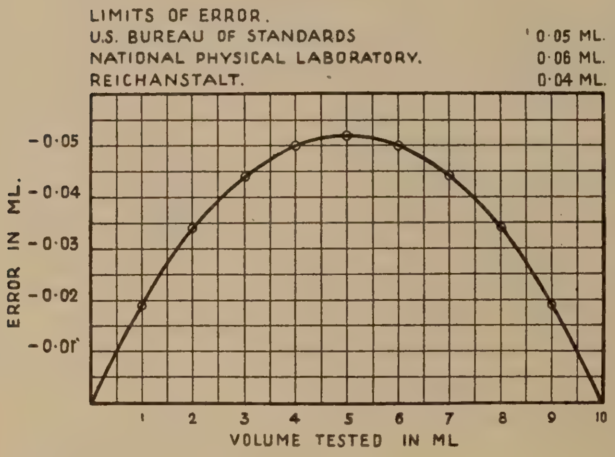

FIG. 2.

It is evident from the foregoing that a burette, correct at the points of calibration, may be in excess of the permissible limit between these points. If the capacity of five intervals is tested and these intervals correspond with the five points of calibration, it is possible that the burette will be certified as correct.

The National Physical Laboratory has lately issued a regulation that burettes are to be tested at any five points and not necessarily at five fixed intervals. This is a significant illustration that the existence of error between the points of calibration is not considered by any means improbable.

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[1] H. V. E. M. Renn, *Ind. Chem.*, **2** [12], p. 33.

(c) Delivery Time Another source of error in burette calibrating concerns the delivery time. The delivery time of a burette is understood to be the time occupied by the unrestricted outflow of water from the zero mark to the lowest graduation. The delivery time of a burette regulates the quantity of water delivered. Again, owing to the drainage of liquid down the walls of the burette, the reading obtained varies according to the time which elapses between closing the tap and taking the reading. Investigations upon this question were carried out by Osborne and Veazey who observed the rise of the water level in a burette after a definite length had been emptied. The amounts of drainage were then plotted against the time intervals. The conclusions of the investigators are summed up in the following extract:[1]

> By limiting the rate of outflow the residue and the afterflow may be made negligibly small. The system of curves considered with reference to the rate of outflow enables a choice of outflow rate which shall sufficiently limit the afterflow. For the maximum or initial rate of outflow a value was sought which should render the residue and the drainage so small that the volume delivered should be independent of such variations and manipulations as are often found necessary by the chemist. Reference to the curves shows that for an initial rate of 0.7 cm per second the maximum drainage from any interval emptied which occurs during the first two minutes after stopping outflow is about 0.05 mm.[2] This initial rate was selected, and the specifications in regard to time of outflow of the total graduated length were so chosen, that on burettes of customary proportions the maximum initial rate should not exceed 0.7 cm/sec.

The existing regulations at the Bureau of Standards, respecting the times of outflow are based upon the observations of Osborne and Veazey.

The delivery time and draining of burettes was made the subject of investigations at the National Physical Laboratory by Stott.[3] A 50 ml burette was used of 534 mm graduated interval and a series of jets was prepared each capable of giving a different delivery time. The results are reproduced in Fig. 3, the amount of water which drained down from the walls of the burette being plotted vertically, and the drainage time horizontally. The delivery times given by the jets used for each set of observations are shown against the curves to which they relate. The drainage was observed after the outflow had ceased.

Reference to the curves will show that when a burette is allowed to deliver its contents quickly the quantity of water draining down the walls is large in comparison with the degree of accuracy required. When the time of outflow was 20 seconds, a volume of 0.24 ml drained down in half an hour, and even in the first two minutes the amount of drainage was 0.07 ml, that is, 0.02 ml in excess of the tolerance allowed by the Bureau of Standards on a 50 ml burette. The delivery time suggested by the writer as suitable for the calibrating apparatus shown in Fig. 1, was 150 seconds, this being the approximate mean of the standard limits. When this time is given, the subsequent drainage is shown by the curves in Fig. 3 to amount to less than 0.04 ml in half an hour. The amount of water which drained down in the second minute of the drainage period was approximately 0.001 ml.

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[1] Bur. Stand., *Bull.*, 1908, p. 584.

[2] That is, a rise of 0.05 mm of the meniscus.

[3] *Jour. Soc. Glass Tech.*, **7**, 175 (1923).

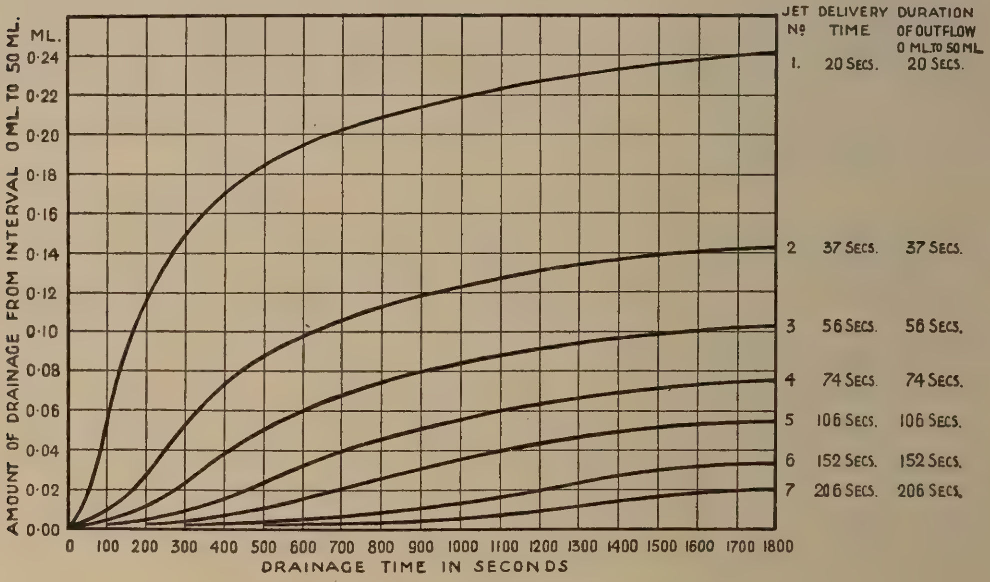

FIG. 3.

The curves amply illustrate the fact that the longer the delivery time, the smaller the probability of error due to such variations and manipulations as are often found necessary in practice. This source of error was also made the subject of investigation by Stott.[1]

A burette of 150 seconds delivery time was emptied in a number of different ways. For example, it was emptied freely from the zero point to the 37.5 ml mark and the tap closed for five seconds. The tap was then fully opened and the water run out to the 50 ml mark. The results obtained by varying this procedure in a number of different ways are shown in the following table.

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[1] *Loc' cit.*

Delivery of burette, 150 seconds
Observed capacity = 49.996 ml = V

Method of emptying	Volume of water delivered, V^1 ml	$(V^1 - V)$ ml
50 ml	49.996	—
37.5 ml + 12.5 ml	50.001	+0.005
37.5 ml + 2.5 ml × 5	50.000	+0.004
25 ml + 25 ml	50.001	+0.005
12.5 ml × 4 times	50.001	+0.005
5 ml × 10 times	49.999	+0.003
2 ml × 25 times	50.014	+0.018
1 ml × 50 times	50.016	+0.020

The same observations were made with a burette the delivery time of which was 31 seconds and a comparison of the two sets of results will show that the liability of error is greatly increased when the delivery time is short.

Delivery time of burette, 31 seconds
Observed capacity = 49.949 ml = V

Method of emptying	Volume of water delivered, V^1 ml	$(V^1 - V)$ ml
50 ml	49.949	—
37.5 ml + 12.5 ml	49.954	+0.005
37.5 ml + 2.5 ml × 5	49.954	+0.005
25 ml + 25 ml	49.956	+0.007
12.5 × 4 times	49.957	+0.008
5 ml × 10 times	49.962	+0.013
2 ml × 25 times	50.003	+0.052
1 ml × 50 times	50.041	+0.092

(d) Incorrect Marking of the Meniscus

Error due to the faulty marking of an accurately measured volume of liquid may arise from the incorrect location of the lowest point of the meniscus, or from parallax. It is evident that an accurate means of measuring a required volume of liquid is useless when it is not coupled with an equally accurate method of locating and marking the position of the water meniscus. When the location and marking is carried out by the eye and hand, unaided by any mechanical device, it is an extremely simple matter to misplace the mark by such an amount as to introduce an error in excess of the tolerance allowed. Parallax, unsteadiness of the hand, uncertainty, general carelessness and "personal factor" will easily account for errors of such magnitude.

A device for the elimination of error due to incorrect location and marking of the meniscus has been proposed by English[1] and is shown diagrammatically in Fig. 4.

A short focus telescope, *A*, working up and down the stand, *B*, by a rack and pinion can be adjusted so that the cross-wire coincides with the extreme point of the magnified image of the meniscus. With a magnification of three or four diameters, it is an easy matter to make this adjustment very exactly without any possibility of parallax error. When this is done, the position is marked on the tube by means of the needle, *C*, which can be moved forward and horizontally, but not vertically. The needle, which is pivoted near the front of the telescope, is pressed forward until its point meets the tube, and is then moved across the tube thus making a fine mark through the India ink, or whatever medium is used for the purpose. As the point of the needle is in the same plane as the cross-wire of the telescope, it is impossible to place the mark in the wrong position.

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[1] *Loc. cit.*

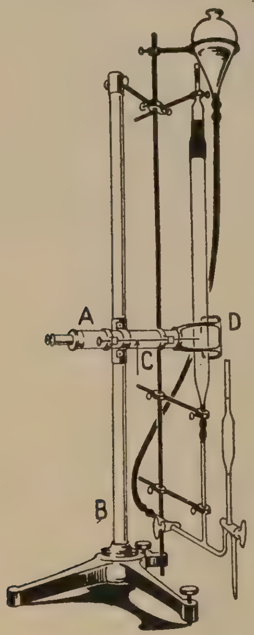

Fig. 4.

It is a well-known fact that in reading a meniscus, the reflections and refractions which occur at the liquid surface and the glass surfaces render the exact location a matter of great difficulty, and that it is necessary to screen and shade the meniscus with some suitable device. Bergmann and Göckell[1] introduced a device that is now universally used in some form or other. It consists in a wooden test-tube holder painted a dull black inside, a square of matt paper being used as a background or screen. The test-tube holder is clamped to the vessel so that its top edge is not more than 1 mm below the lowest point of the water meniscus.

The Bureau of Standards requires the following method of reading:

> In all apparatus where the volume is limited by a meniscus the reading or setting is made on the lowest point of the meniscus. In order that the lowest point may be observed it is necessary to place a shade of some dark material immediately below the meniscus, which renders the profile of the meniscus dark and clearly visible against a light background. A convenient device for this purpose is a collar-shaped section of thick black rubber tubing, cut open at one side and of such size as to clasp the tube firmly.

At the National Physical Laboratory, a strip of black paper is folded round the circumference of the vessel not more than 1 mm below the mark on which the setting is made and held in position by an ordinary paper-clip. The meniscus thus shaded is viewed against a white background.

In the device shown in Fig. 4 when using a telescope for fixing the position of a magnified meniscus, it is not only necessary to use the same screen, but also that this screen should be kept the same distance away from the tube, as a variation in the distance between the screen and the tube, very appreciably affects the apparent position of the meniscus. To prevent error from this cause, a screen, *D*, is mounted on a framework which is secured to the telescope tube and thus a permanent background is provided at a fixed distance behind the tube being calibrated.

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[1] *Z. angew. Chem.*, 829, 990 (1900), 4 (1902).

The device outlined above, used in conjunction with the measuring apparatus suggested by Stott (Fig. 1) successfully eliminates serious errors in the calibrating operation.

(e) After-Working of the Glass

A source of error that is not sufficiently recognized is the occurrence of after-changes in the glass during a period immediately following manufacture. The first work to appear on the subject was that of R. Weber,[1] who made observations upon 23 different thermometer glasses with a view of establishing a relation between the after-workings of a thermometer and the composition of the glass.

If a newly-made thermometer is merely exposed to variations of atmospheric temperature the glass gradually contracts, the movement slowly decreasing until it finally ceases. With some glasses variations continue to occur even after a period of years, but the experiments conducted by the present writer upon glass volumetric apparatus show that a period of seven months is usually sufficient in order to avoid excessive error.

The theory put forward to explain the phenomenon of after-working is still open to question. Upon the release of stress, such as would occur in the ordinary process of annealing, an elastico-viscous movement is set up which may extend over a comparatively lengthy period. During the fall of temperature, the walls consist of layers at different temperatures. If these layers are considered, for the sake of argument, to be independent of each other, they would separate from one another, the distance being proportionate with the differences of temperature and with the expansibility of the glass. As soon as the layers have attained a common temperature they will all be in contact and free from stress. As the layers are not independent, however, but are actually united firmly together, it follows that during the fall of temperature, a deformation occurs, the outer and inner layers being under stress, while between the two there will be a layer free from either thrust or pull. The elastic deformations thus produced in the walls during the change of temperature are responsible for the phenomenon of after-working. As a working hypothesis, it has been assumed[2] that there is an alternate inward and outward movement as the results of the two opposite kinds of stress which contend with one another. An increase of temperature was chosen for the hypothesis. Upon an increase of temperature, the after-working of thrust in the outer layers first comes into operation. The movement continues beyond the normal equilibrium and the after-workings of pull in the inner layers come into play. The limit of this movement will depend upon the magnitude of the movement itself and upon the elastic resistance of the outer layers. After the movement of extension has ceased, there will be slow recoil, and the after-working of pull finally ceases, but this time without stress in the walls.

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[1] Ber. d. Berlin Akad., 1883.

[2] Hovestadt, Jena Glass.

It is evident from the foregoing that the minimum after-working is brought about when the conditions are low thermal expansion, high conductivity, and high coefficients of elasticity. Weber[1] concluded from his investigations upon the relation between after-working and composition that the very fusible alkali glasses give bad results. A good result is given by pure potash glasses with large proportions of silica and lime. This conclusion was later confirmed by Wiebe,[2] who showed that after-working is most pronounced in glass containing soda and potash in about equal proportions and that in a potash glass nearly free from soda the after-working was least. The amount of lime ranged from 7 to 14%. The results of experiments carried out at Jena show that, in general, glasses possessing good thermal endurance are least affected by after-workings.

In the experiments conducted by the present writer to determine how after-working affected the accuracy of glass volumetric apparatus, a soda-lime glass was used containing a small proportion of potash. In the first experiment, five flasks of 100 ml capacity were marked with a fine line around the circumference of the neck. The capacity was then computed from the results of three determinations, each determination being carried out by an independent observer. During the seven months that the vessels were under observation, the temperature varied over a range of less than 10°C. Drying was carried out by first rinsing with alcohol and ether and then passing a stream of air through the flask by means of an ordinary filter-pump. The flasks were examined optically for strain and were found to be well annealed. Tests were made each month by three independent observers and the alteration in capacity computed from the mean of the determinations. The results have been recorded graphically in Fig. 5.

It will be seen that in every case a sudden contraction, ranging from 0.006 ml to 0.024 ml, took place in the first month. During the second month the contraction considerably diminished in magnitude, the greatest alteration, 0.008, being observed with the two flasks numbered 2 and 3 respectively. The third month showed that the diminution in volume was still less, flask No. 2 showing the greatest contraction with 0.006. In the case of flask No. 4, a slight increase in capacity was observed. This expansion was noted with four out of five flasks at some time or other during the period of test, the one exception being flask No. 3. Unfortunately, this was broken during preparations for the tests after the fourth month, a fate which also befell flask No. 4 two months later. The slight increase in volume noted in the four cases is most probably due to some experimental condition and the writer would not suggest that the increase was real. It was not until after the fourth month that the curves began to approach more nearly straight lines and it is evident from this that, for the particular glass employed, a standing period of five months before calibration should be the minimum allowed. As a matter of fact seven months was decided upon as the most suitable period.

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[1] *Loc. cit.*

[2] Ber. d. Berlin Akad., 1884.

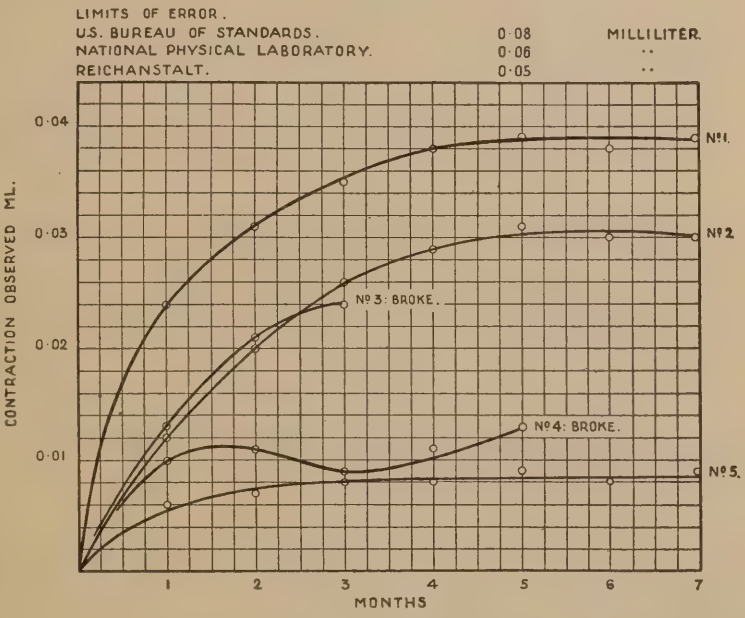

FIG. 5.

A flask can, of course, be graduated during the period of contraction and still be within the limits of error allowed, after the movement has ceased. This is easily possible if the capacity of the flask is slightly larger than intended, for the alteration in volume due to shrinkage would bring about the cancelling of the original error. In cases where the original error is of minus value, however, it is not improbable that the diminution in the volume of the flask due to after-working would cause the error to be increased beyond the permissible limits.

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REFRACTORIES FOR OIL-GAS MANUFACTURE[1]

H. J. Knollman[2]

ABSTRACT

The present investigations of refractories by the oil-gas industry on the Pacific Coast were stimulated by sporadic independent tests in the past whereby it was observed that different qualities of fire brick not only had varying lengths of service but also had an apparent influence on the amount and quality of gas made and on the efficiency of gas manufacture.

The essential differences in generator design, including that of brick-work construction, in the two-shell type of generator as compared with the single-shell generator are such that longer refractories life is obtained in the former type. The operations in the manufacture of oil gas for the two-generator types are briefly discussed, showing that the refractories are subjected to alternating oxidizing and reducing conditions.

Other causes contributing to ultimate refractories failures are carbon deposition in the brick, abrasion of hot gases and the impinging of long flames on the brick, heavy checker-brick loads on arches, faulty construction of arches, and erratic working conditions. In addition, super-saturated steam, heavy hydrocarbons, and salts and sulphur in the oil, are contributing causes to checker-brick disintegration, especially in the generator zones where the oil and steam are introduced. It is hoped that specifications for refractories may be drawn up from the results of practical service tests now being conducted.

The heat-transfer and heat-absorption properties of various refractories, such as conductivity, specific heat, density, diffusivity, heat capacity, and time required for the refractories to reach near-heat saturation, are discussed, particular attention being given to their possible application as oil-gas generator checker brick. The need for more complete and accurate data on the fundamental constants necessary in heat-transfer calculations is pointed out.

Researches on refractories with thermal properties superior to fire brick are now being conducted in generators in an endeavor to increase gas capacity and operating efficiency along the lines indicated by theoretical considerations.

Introduction

The important part that refractories play in the process of making artificial gas from crude oil or its residues as carried out in the oil-gas industry is being increasingly realized by the utilities in question. The oil-gas industry, with the exception of a few small installations in the East, is confined entirely to the Pacific Coast, extending essentially from Portland, Ore., in the north, to San Diego, Calif., in the south. For this reason its refractories problems have been of a rather local nature; and since initial cost combined with past performances have been the criteria by which purchases were made in the past, but little attention has been paid to the special requirements of gas-plant refractories.

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[1] Published by permission of the California Gas Research Council. Presented at the Annual Meeting, American Ceramic Society, Atlanta, Ga., Feb., 1926. (Refractories Division.)

[2] Ceramic Engineer, Los Angeles Gas and Electric Corporation, Los Angeles, Calif.

This attitude has been gradually changing in the last few years, however, so that more attention is being given to the matter of adapting refractories of distinct characteristics to the purpose for which they are best suited, and to buy on the cost-plus-service rather than on the initial-cost basis.

The condition that has existed in the past may be said to be due in part to several reasons: (1) the quality of the refractories varies sufficiently from time to time to make it difficult or impossible to secure accurate data; (2) the generator operating conditions are not sufficiently uniform to give the refractories a fair trial under any particular conditions; (3) the large variety of generator sizes and their variable dimensions, with consequent variations in operations as found in the different companies of the industry, make it very difficult to obtain systematic and definite refractories data; (4) the grouping together of a number of generators in the same plant, few of which are independent of each other, results in operating figures that give only the average results for the whole plant, and it is therefore difficult to compare the behavior and relative efficiency of one generator with another.

1. First Practical Tests on Refractories

The first concerted effort to pay greater attention to the refractories required was made by the Joint Committee on Efficiency and Economy of Gas of the Railroad Commission of the State of California. This Committee was later reorganized as The California Gas Research Council, under whose direction the present research work of the California gas utilities is being conducted.

The original Joint Committee made extensive researches and plant tests during the years 1920 to 1923 to determine the efficiency of gas production at existing gas plants and under existing modes of operation for the production of different qualities of gas. During the course of these researches the Committee's attention was frequently called to the apparent influence of various fire brick on the amount and quality of gas produced and on the efficiency of gas manufacture. Consequently in their Progress Report of September 15,1 921, the following clause will be found:

> Little is known at the present time regarding the quality of checker and lining brick as adapted to gas generator use. Utilities in the State have found no definite method of determining beforehand the probable usefulness of different bricks. The determination of a practical means of testing fire brick to be used, and the type of brick best adapted to gas use, is to be studied for the benefit of the industry.

This Committee sent out a questionnaire to the principal oil-gas companies requesting data on lining and checker brick, spacing of the latter, and specifications. The answers received showed that there were no specifications, but that there were considerable variations in length of service and in desirable properties of the brick required, with no accurate data as to the reasons for the variations and differences of opinions expressed.

In order to study the respective merits of different checker brick, this Committee secured fire brick from four different refractories manufacturers, two located at Los Angeles, one at Stockton, Calif., and the fourth at Denver, Colo. These brick were installed in a gas generator at Santa Barbara, Calif., in June, 1922, and were laid straight flue with 2½-inch spacings between the brick, in such manner that each representative brick was allotted a one-quarter vertical section of the total checkers.

Due to some unusual conditions, the operation of this generator soon became very erratic, and it refused to respond to any of the usual methods of regulation and control. Various cycles were run under different variations of blast and heat, the effect of which showed an extremely unbalanced thermal condition of the gasifying zones. Wide variations in the quality of the manufactured gas were obtained, accompanied with difficulty in diffusing the heat from the combustion chamber uniformly throughout the checker brick. On account of the uncontrollable tendency of the generator to cause wide fluctuations in the heating value of the gas, together with an excessive oil duty, it had to be taken out of service after about a month's trial. The unsatisfactory heat conditions for gasifying the oil were attributed to the different properties of the bricks under test. This view was strengthened by later results, when the different brick were used independently in the generators without such untoward results, but with varying efficiencies.

2. Present Investigations of Refractories

The references and conclusions on fire brick made by the Joint Committee aroused such interest in the refractories problem that the California Gas Research Council has continued the investigation as one of its major research projects, working in close coöperation with the committees of the Pacific Coast Gas Association. The Pacific Coast Gas Association has now a Refractories Bureau, with H. L. Masser, Gas Engineer of the Los Angeles Gas and Electric Corporation, as Chairman. This Committee is composed of three subcommittees, known as the Refractories, Checker Brick, and Insulation Committees. The subcommittees at the present time are composed of representatives from the various gas companies and from various interested California refractories manufacturers. Their object and purpose is to make tests and service studies of their respective particular refractories problems, in order that the special requirements of the industry may be determined and be more definitely understood by both the consumer and the manufacturer. Proposed refractories studies, as well as those already under way, will be discussed at greater length in the latter parts of this paper.

Oil-Gas Generators and Their Operation

There are two distinct types of oil-gas generators in general use: the single-shell or "straight shot," and the two-shell or Jones generator. The latter consists of two cylindrical steel shells or chambers, primary and secondary; whereas the former consists of one cylindrical vertical steel shell. Both types are lined to a greater or less degree with some form of insulation next to the steel, followed by one or two courses of fire brick, which make up the generator side walls.

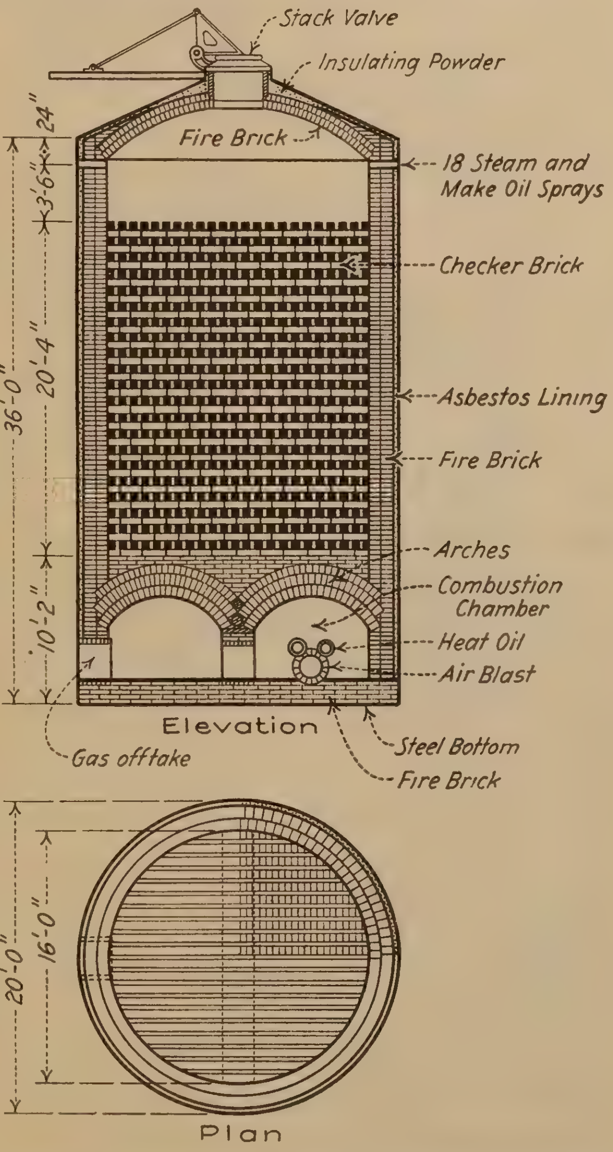

FIG. 1.—20-foot diameter single-shell straight-shot oil-gas generator.

1. Construction of Single-Shell and Two-Shell Generators

Figure 1 shows the essential construction features of the single-shell generator. The steel bottom is covered with several layers of fire brick, or with insulation and fire brick. There are two long combustion chambers at the bottom of the generator separated by a firebrick center wall with arches overhead. The arches, consisting generally of three separate rings laid one directly over the other, are spaced about 3 to 4 inches apart, thus allowing the hot gases to pass on up between them. They support the mass of checker brick overhead. The checker brick generally consist of standard 9-inch brick, spaced from 2½ to 3½ inches apart in regular checker fashion, thus leaving open checker spaces through which the gases can travel. Above the checker brick is another open space, occupying one-third to one-fourth of the interior of the generator, which is the gas-making chamber. The roof consists of fire brick on the inside of the gas chamber, with loose insulation between the fire brick and the steel roof on the outside.

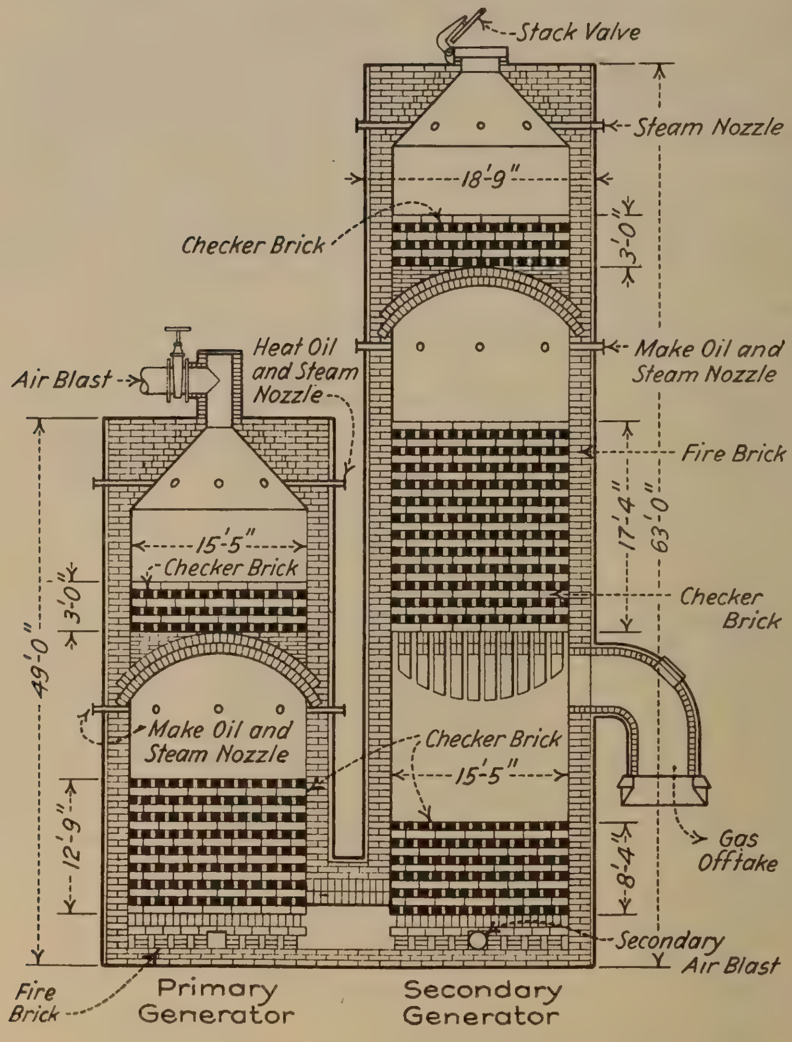

Fig. 2.—18 ft. 9 in.-diameter two-shell oil-gas generator.

Entering the two combustion chambers at the bottom are blast pipes, admitting air for combustion, and burners for conveying the oil for heating. The heating is accomplished by means of a long flame burning throughout the length of the combustion chambers. Entering the upper chamber above the top checker brick are a number of steam and oil sprays for gas-making purposes. On the top is the stack valve, open while heating and closed while making gas.

Figure 2 shows the essential construction features of the Jones generator, where the primary and secondary shells are connected at the bottom with a steel throat piece lined with fire brick. The side walls and bottoms are lined with fire brick and insulation, but the interior arrangement consists of open chambers and bodies of checker brick alternated at different heights in the two shells. Each shell has a body of checker brick on the bottom followed by an open chamber overhead. In the primary shell, arches are built in the upper section of this lower open chamber. These arches support 4 to 6 courses of checker brick overhead. This checker work is then followed by another open chamber. In the upper part of this chamber are located the heat oil and steam nozzles. The heating up of both shells is accomplished at this point. A stack with air blast completes the top of the primary shell.

The secondary shell has the gas off-take in the first open chamber above the bottom checkers. A large number of checker brick supported by arches with suitable openings between them are located in about the middle of the secondary generator. Then follows another open chamber with provision for make-oil and steam nozzles. Arches are located in the upper section of this chamber, which in turn support four to six courses of checker brick. An open chamber with the stack on top and provision for steam nozzles completes the top of the secondary shell. At the top of the primary shell and the bottom of the secondary shell are inlets where air is introduced.

Single-shell generator sizes range from 5 feet in diameter by 18 feet high to 27 feet in diameter by 43 feet high; while the two-shell generator sizes range from 3 feet 6 inches in diameter, with a rated capacity of 40,000 cubic feet per day to those 18 feet 9 inches in diameter, with a rated capacity of 5,000,000 cubic feet per day. The single-shell generators have a rated capacity ranging from 100,000 cubic feet to 5,000,000 cubic feet per day. The largest size of both types of generators requires in the neighborhood of 60,000 standard 9-inch checker brick.

2. Operation of Single-Shell and Two-Shell Generators

The gas-making operations, while essentially the same, vary considerably in the two types of generators, principally due to the fact that more water gas is made in the two-shell generator. The heating and gas-making periods of the cycle also vary with the size of the generator so that the operation of an average-size generator of each type will be briefly discussed.

In the average-size single-shell generator the stack valve is opened at the end of the make period; the air-blast valve at the bottom is then opened and air turned into the generator. This part of the cycle, known as the dry blast, lasts from one to three or four minutes, and often is accompanied by long flames through the checker work. The operator dry blasts the generator in order to clear it of waste gases and to burn away excess carbon deposited on the checker brick from the previous run. He next turns on the heating oil, which is sprayed into the bottom combustion chambers where, mixing with the air, it ignites and burns with a long flame, the hot gases meanwhile passing up between the arches and through the checker brick and making chamber, finally leaving through the stack. This part of the cycle usually lasts from 9 to 12 minutes. The dry blast and combustion period together constitute the heat period. The checker brick are thus heated to an average temperature of 1700°F.

Following the heat period, the blast and stack valves are closed, and then oil mixed with steam in a finely divided state, which is generally preheated to a few hundred degrees, is sprayed through the injector nozzles into the making chamber at the top of the generator. Upon striking the heated checker brick, the finely atomized oil and steam are converted into gas. The gas passes down through the checker brick and leaves the generator through the off-take pipe at the bottom of the generator, whereupon it then goes to the washbox and remaining purification processes before finally reaching the gas holder.

This conversion of oil and steam to gas lasts for about 15 to 25 minutes, when the checker brick have then become so cold that they must be reheated. The generator is then purged for 5 to 10 minutes with steam so as to drive out the remaining gas left in the generator after the oil valves have been closed. This purge period combined with the period of conversion of oil to gas is known as the make period of the cycle.

In the two-shell generator the gas off-take valve is closed and the stack valve opened at the end of the make period, whereupon the operator then turns on the air blast at the top of the primary generator. This dry blast, lasting for a few minutes, clears the generator of the waste gas from the previous run and burns the carbon on the checkers. The heat-oil and steam-nozzle valves located in the upper chamber of the primary shell are then opened, whereupon the superheated steam and oil mix together through the burners, the steam breaking up the oil so that the mixture of the two is in a finely divided state. The oil-steam spray mixes with the air introduced by the blast through the stack and ignites, so that combustion rapidly takes place. The hot gases pass down through the primary shell, across through the throat connection and up through the secondary shell. The waste products of combustion finally pass to the atmosphere through the secondary shell stack. The heat period, together with the dry blast, lasts for about 10 minutes, heating the checker brick to an average temperature of 1600 to 1700°F.

The generator is then ready for gas making. The operator first closes the air blast, then opens the off-take valve and closes the stack. Then for about a minute he turns steam into the upper open chamber of the secondary shell. Next he opens the valves which allow the steam and oil to flow through the nozzles. The oil, usually preheated, is sprayed upon the heated checker brick, whereupon it is immediately changed from liquid to gas. The steam combines with the oil gas, similar to a water-gas reaction, to form the manufactured gas. Gas making goes on in both shells of the generator at the same time. From the open chambers, into which the oil and steam are sprayed, the gas passes between the hot checker bricks to the off-take chamber. It travels down through the primary shell, across the throat connection, and up to the off-take, while on the secondary side it travels down from the making chamber to the off-take below. This conversion of steam and oil to gas lasts from 8 to 10 minutes. The generator is then purged for a few minutes with steam in order to drive out the remaining gas left in it, and it is then ready for the dry blast.

3. Alternating Oxidizing and Reducing Conditions

From the nature of the process, it will be seen that both the arch refractories and the checker brick are subjected to alternating oxidizing and reducing periods, in which the latter condition strongly predominates. During the heat period, the gases may become highly oxidizing. An average gas analysis taken near the end of the heat period is as follows:

CO_2	13.0	O_2	2.0	N_2	85.0

During the make period the refractories are not only subjected to a large amount of finely divided carbon particles, but also to the intense reducing gases made during this period. The following may be considered a typical average analysis of the manufactured gas after its purification:

CO_2	2.0	CO	10.0
C_nH_{2n}	1.5	CH_4	40.0
O_2	0.2	N_2	1.5
H_2	45.0		

Due to the regular cycles of operation of the generator, the heating and cooling of the refractories is in regular cycles, but at irregular rates. The temperatures within the generator and the rate of the temperature rise and fall is not known to a high degree of precision. This is mainly due to the fact that serious difficulties are encountered in making temperature observations within the generators themselves. The heavy deposits of carbon, and the intense reducing gas conditions, especially at the higher temperatures encountered above 1700°F, alter the potential of both base-metal and rare-metal thermocouples in a very short time. High-duty alloy steels are required for protection tubes, and even they are permeable to the gases and have a rather limited life under the deposition of carbon and strong reducing conditions of the gaseous atmosphere at these higher temperatures. The problem of suitable pyrometric equipment for use in oil-gas generators with a reasonably long life and accurate temperature readings for long periods of time is not as yet completely solved.

Refractories in the Combustion Zone of Generators

1. Comparison of Life of Refractories in Two Generator Types

Some of the refractories, such as those used for the dome arches, stack nozzles, and side-wall linings, are under such comparatively mild working conditions that their repairs are insignificant, and they have an almost indefinite life in all generators. The refractories for arch use are under much more severe conditions, however, particularly in the single-shell as compared with the two-shell generators. Not only are the former subjected to excessive flame conditions, due to the large amount of checker brick overhead that have to be heated during the heat period of the cycle, but they are also subjected to a much greater load than similar refractories for arch use in the two-shell generators. In the one case, the refractories subjected to intense heat conditions carry practically no load, while in the other case the arches are subjected to intense heat, and also support the entire column of checker brick used in the generator. Failure of the arches in the latter case causes the entire checker work overhead to fall in, so that the refractories requirements are rigid under such conditions.

Information submitted by the various gas companies in a questionnaire have shown that not only the refractories but also the checker-brick life have been much longer on the average in the two-shell type of generator. The life of the checker brick in a single-shell machine averaged about 18 months as compared with 30 months in the two-shell type. The difference is largely due to the failure of the arch brick, causing losses in the checker brick, either from the arches falling down or from the handling losses of the checker brick when new arches have to be installed. In general, the companies using the single-shell type experience more trouble with the arches than with the checker brick. Because of this, particular attention is being paid to the refractories requirements for arch use as found in the single-shell type of generator.

2. Refractory Requirements in the Combustion Zone

The refractories located in the fire boxes of the single-shell generators are therefore subjected to the most severe conditions. In general, the temperatures are not excessive, that is, the average temperatures are greatly under 3000°F. Unfortunately, however, the temperature is generally not uniformly distributed, so that the refractories in some sections of the fire box are subjected to excessive localized overheating and to flame temperatures, while other sections are favored. Uneven or excessive heat distribution is also caused by forcing the generator to utmost capacity during peak demands for gas, or to accidental causes such as fallen checker-brick sections overhead. Some of the refractories are therefore subjected more or less regularly to a flame temperature exceeding 3000°F, so that brick of high refractoriness are then required.

In many instances improvements in burner design or in location of burners in the fire boxes are of distinct benefit in increasing the life of the refractories. The burners are often so situated that their flame plays directly upon some section of the arches or side walls, particularly under forced conditions whereby the flame length is materially increased, with the result of excessive glazing, spalling, or actual melting at that point. Equalizing the temperatures in the combustion chamber and preventing the flame from being continuously in contact with the refractories during the heat period results in distinct economies. Inspection of various generator fire boxes has plainly revealed these conditions, showing where some of the side-wall and arch brick are heavily glazed and partially melted; whereas in other sections where the flame never comes in contact with the fire brick, they are but little affected beyond surface discoloration, even after months of service.

Where long exposed to excessive flame action, failure of arches results. If an arch has been partly burned away unevenly so that it is thin on one side while the other side retains its original thickness, its stability is endangered so that a collapse is threatened. This would be more noticeable and pronounced were the arches constructed of but one circle of brick; but since three circles are generally used, the upper ones help to carry the major portion of the load and are exposed to much less rigid heat conditions, so that failure of arches is rare. The factor of safety is thereby very materially increased.

The rise of the arch is also a matter of importance. The tendency in recent years has been to increase this rise, so that a rise of 20% of the span is now found in the larger and newer generators. The radius of curvature of the inside of an arch is commonly made in a great many furnaces equal to the span, which makes the rise equal to 13.4% of the span. Several instances have been recorded where arches have collapsed with the entire checker work overhead when too flat an arch was used. Because of the uncertainty of the various factors involved, a considerable factor of safety in arch construction is deemed advisable, which is obtained by the common practice of high arch rises and multiple circles of the arches.

This manner of construction has, to a large extent, prevented deformation of the arch brick due to softening under heat. Any excessive glazing and softening of the brick is confined almost altogether to the lowest circle; and since the other two circles still carry the major portion of the load, plastic deformation of the refractories is not greatly in evidence, even though excessive glazing or melting, so that the brick start to drip, may have taken place on the lower circle. In fact, repairs are invariably necessary on the lower circle of arch brick only, while the upper circles may last several years before it is necessary to completely remove them, the exact length of service depending largely upon the severity and extent of use during the comparatively short winter seasons. The center and side walls in the fire boxes are so large and massive that they do not need serious consideration, even though portions of the walls may be subjected to severe conditions of use.

3. Spalling Spalling of refractories in oil-gas generators is a matter of practical concern and often is of more serious consequence than refractoriness. In many instances, severe spalling takes place, and it is generally greatest where the temperatures are the highest. Owing to the intermittent nature of the generator operation, whereby the refractories are rapidly heated up during the heat period and are then cooled during the gas-making period, favorable spalling conditions are present. The long oil or gas flames impinging only at periodic intervals on the refractories present a severe condition, difficult to overcome. Add to this the alternating comparatively short oxidizing conditions during the heat period, followed by intense reducing conditions for a much longer period of time, and it will be seen that most favorable spalling conditions are present, which are a serious factor in affecting the ultimate life of the refractories.

The refractories absorb a large amount of finely divided carbon under the reducing conditions, which, upon being oxidized, expands in volume, tending to disrupt the brick. Moreover, the action of the reducing vapors on the fire brick brings about a volume change on the exposed portions of the brick by causing incipient vitrification. Such fire brick become glassy and changed in character, due mainly to a reduction of the fluxes in the brick, so that reduced silicate slags are formed. The result is a cracked brick surface or spalling, which has a weakening effect on the entire arch structure. The brick pieces fall to the floor, and the margin of utility of the brick in the arch is materially lessened. Examinations made of badly spalled brick have readily disclosed sections of the same brick in various stages of incipient vitrification, accompanied by cracked brick surfaces.

A common practice that partially overcomes this condition is to wash or paint the brick surface with a mixture, such as common salt or clay, that will fuse and glaze the surface. The pores are thus sealed so that the reduced gases are not so readily absorbed. Although lowering their refractoriness somewhat, this is confined to the outer section of the brick and is preferable to the excessive spalling otherwise taking place. This practice is extensively employed in the industry with greatly improved results, although more refractory glazes, which have a melting point as high or higher than that of the brick themselves, are now being tried out in tests. A refractory glaze coating, sealing the pores but containing only enough fluxing material to attack slightly the surface of the brick upon which it is applied, so that it becomes practically a part of the brick, gives evidence of being much more desirable.

4. Causes of Refractories Failures The principal causes of destruction of fire brick under operating conditions are the deposition of carbon within the bricks from the volatile hydrocarbons, the abrasion of hot gases and impinging of long flames on the brick, expansion and contraction of the brick due to sudden temperature changes, and in some instances the pyrochemical action of solids, salt water, sulphur, etc., present in the oil. Often also a generator which has been lying idle for a considerable period of time is suddenly pressed into service at maximum capacity. This is a condition that has to be contended with during the winter seasons in order to meet peak gas load demands.

5. Final Selection and Construction Factors Involved In general, the most suitable firebox refractories are low in fluxes so that their refractoriness is increased; heavily grogged, of coarse grain, to reduce spalling; and preferably fired to a high temperature to reduce danger from excessive shrinkage and cracking later in use. Where not exposed to flame conditions a moderately refractory fire brick serves adequately, particularly for generator side-wall use.

The value of having skilled workmanship in laying up the refractories is, in general, fully realized. Badly laid masonry results in the best of refractories having an inferior life, as has been demonstrated by actual failures. Fire brick, especially for arch use, must be true to shape—a requirement to which special attention is being given. Deformed brick with high or low spots take unequal stresses when in use and are subject to cracking because of undue strains on the high points. The brick are commonly set rubbed in place, and if mortar is used between them at all, they are dipped in a thin refractory fireclay mortar. Thick mortar is now quite generally avoided in the industry, and much better results are obtained by using the mortar very thin and by using a fire clay or a mixture of fire clay and finely ground grog of refractoriness equal to that of the brick themselves. Since the sizes of arch brick in general use are special wedges, usually nine by six inches, with varying maximum and minimum thickness, not much cutting is necessary, and this is avoided as much as possible. Considerable attention is paid to proper workmanship by skilled masons, well versed in laying up refractories.

6. Present Service Tests Some practical service tests are now being conducted in an actual generator in preference to depending upon the results of laboratory tests. The problem of the specification of refractories in the combustion zone of a generator is a difficult one because no laboratory tests are available which in any way serve to give a comparison with that obtained in commercial operation. The available load tests, water or air spall tests, shrinkage and high-melting-point tests, are inadequate, inasmuch as it is almost impossible to obtain the gaseous atmospheric condition that is present in the generator during the processes of gas-making. A modified load test is misleading and inconclusive, since the temperatures under normal operating conditions are so variable and are generally lower than called for by the test, and the loads are also variable in different sized generators. The most conclusive test is, of course, secured by actually installing the various refractories in the generator arches, and having them carry the normal checkerbrick load overhead.

Several Pacific Coast refractories manufacturers have submitted their representative fire brick for test, and these have been installed in a large generator at the plant of the Los Angeles Gas and Electric Corporation under normal operating conditions and normal loads. The brick for the test were as uniform in shape as was commercially possible to make them, and they were laid up with very thin dipped joints and rubbed in place.

Since the temperature distribution in the fire boxes is so variable and the upper two rings of any particular arch are under less severe conditions, the upper rings were constructed of one manufacturer's product only; but the lower ring of all the arches in this test generator was laid up with all of the different representative refractories, in regular rotation, so that the various fire brick are being given as nearly as possible the same service conditions. All representative brick under test are therefore being given equally severe to equally moderate service conditions. A careful record is kept of the exact location of each brick. This generator is now in continuous operation, and the necessary manufacturing data is being recorded for later use in correlating results. After the present winter's run, the generator will be laid out, the brick carefully examined, and their respective condition in the various sections recorded for further use.

Several mortars of quite widely varying properties, as well as glaze coatings on the surface of the brick that have been used to prevent spalling in the past, are included in the test. By correlating the service results with the properties, composition, method of manufacture, etc., of the various refractories under test, it is hoped to obtain sufficient data so that specifications for refractories for future use can be drawn up. It is proposed to extend this study to brick of widely varying characteristics and to those manufactured in other localities should the wisdom of such a course be indicated or appear necessary, supplemented by such laboratory tests as will indicate limits of use.

Refractories Requirements in Connection with Generator Insulation

Proper insulation of gas generators in order to prevent heat losses, firing out of steel bottoms, and the like, is claiming the attention of the industry to a constantly greater degree. It is not a matter of special interest here, except as it affects the refractories used in this connection or is affected by them. The usual manner of insulating generators is to employ materials of low conductivity, such as infusorial earth, magnesia, fire felt, glass wool, light-weight refractories, and the like, next to the steel shell, followed by one or more courses of fire brick of good quality.

Since considerable pressure is exerted within the generator against its side walls and exterior during the gas-making operations, the problem of obtaining gas-tight walls is a matter of considerable concern, especially if but one course of fire brick is used and the insulating materials deteriorate at comparatively low temperatures. The opening up of joints, both between the refractories and insulating bricks where the latter are used, largely destroys the effectiveness of insulation, since the hot gases then penetrate through these joints and heat the steel shell, allowing large heat losses. The use of truly non-shrinking, high-temperature cements between the fire brick in order to render the wall as nearly monolithic and gas-tight as possible is a necessity, in which good workmanship in laying the wall also is a large factor. Not all opening up of joints is eliminated by their use under all conditions, owing to the expansion and contraction of the generator walls with variable working conditions, such as frequent temporary shut-downs, variable temperatures in the generators, and the like, but the degree of heat loss is very materially reduced. In a number of instances the use of insulating materials has been rendered rather ineffective due to the opening up of numerous joints in the brick work, especially where excessive quantities of high-shrinking, fireclay mortars were used between the bricks. Close attention to this factor is a necessity if satisfactory results are to be obtained.

Another factor of some influence is the penetration of carbon in the pores of the fire brick. In extreme cases the penetration may become very heavy, or heavy hydrocarbons may be absorbed so that the brick have the appearance of being oil soaked. In certain instances they become oil soaked from direct leakage of oil onto the brick. This carbon penetration reaches the insulating materials, and when it becomes excessive the insulating value of these materials is materially reduced. Dense, hard-fired brick are more effective than soft, porous brick in resisting this penetration of carbon and carbonaceous compounds, so that fire brick of a dense nature are here best used.

Checker Brick

1. General Checker-Brick Considerations The checker brick used in oil-gas generators assume a position of great importance, for in many respects they are the heart of the process of converting crude oil or its residues to artificial gas. The heat absorption, conduction, and heat-transfer properties of the checker brick used play a large part in the efficiency of the process. Interesting and important as are these properties, the physical properties of the brick, such as fusion point, mechanical strength, load-carrying ability, resistance to spalling, cracking, and disintegration, must be given first consideration.

A study of checker brick that have been in continuous use for some time in the average-size generator indicates that they may be roughly divided into two classes: (1) those that tend to become porous, fragile, and weak; and (2) those that become dense and vitreous. The most porous and fragile brick are usually found in the upper courses, whereas the most vitreous, often to the extent of being partially melted, are naturally found nearest the combustion zone. This distinction is not sharp nor well defined; and the upper, more fragile brick often become quite dense due to the fact that the temperatures are sufficiently high to cause partial vitrification of the clay, whereas the oil and steam have exerted a disintegrating influence.

In the single-shell generator, the first few courses just over the arches, and the first few upper courses under the oil and steam nozzles and injectors, bear the brunt of severe operating conditions, but in an entirely different manner, whereas the middle section of the checker work is the most favored. The lowest checker brick must withstand the more severe temperature conditions—at times nearly as severe as the arch brick refractories—and in addition must stand heavy loads, since they support the entire checker-work structure. This does not hold true, however, in all cases for the lower checker brick in the two-shell generator, since they are often far removed from the combustion zone and also do not carry such heavy overhead checker-brick loads. The upper checkers, on the other hand, while under more moderate temperatures, are subjected to quite rapid temperature fluctuations, carry no load, and do the bulk of the conversion of oil to gas, especially at the start of the make period. The middle checkers are under the most favorable operating conditions, since they are free from either one of these extremes and so are most moderately affected during their life in the generator. The upper and lower checker brick must also stand up under abnormal conditions, especially when the generators are forced to meet peak winter load demands. They must therefore be resistant to such conditions as excessive heat, action of steam from leaky injectors, excessive oil, and the like.

2. Lower Checker-Brick Requirements In the single-shell generator, the checker-brick courses immediately over the arches must be nearly as refractory as the firebox refractories and, in addition, must be considerably denser and stronger. Owing to their remoteness from the combustion zone, they are not subjected to severe spalling conditions and so need not have an open structure but rather should be dense and well bonded in order not to warp excessively. Observations on the lower two or three courses of checker brick just over the arches have shown two general classes: (1) those that are so refractory that they glaze with difficulty but warp more or less severely, accompanied with opening up of cracks on the bottom side; (2) those that glaze readily, but do not warp to any extent and show but few cracks. The warping and accompanying cracking of the former class was not primarily due to low refractoriness, but invariably was found to be in the more refractory brick that were composed of hard refractory particles of clay or grog, bonded together with a comparatively small amount of fine-grained bond clay. The latter class, while generally considerably less refractory, were machine made, with little or no grog or coarse clay particles, and so were mechanically stronger under the heat and load conditions and therefore less subject to warping. The ideal brick for this use is a hard-fired brick of a highly refractory nature, bonded with a large amount of fine-grained clay. Since the brick are laid on edge, with a checker spacing 2½ to 3½ inches apart, the transverse strength of the checker bricks used in this capacity must be high. Owing to the importance of their location, brick for this particular purpose demand considerable attention, especially with the increasing tendency to use more expensive checker brick in the generator.

3. Upper Checker-Brick Requirements Since the upper checker brick are subjected to such destructive agents as oil and steam, together with carbonizing or reducing gases, the tendency toward opening up and weakening of the brick structure is pronounced. Super-saturated steam, heavy hydrocarbons, salts, and sulphur in the oil, all have a deleterious action due to chemical reactions or mechanical action on the checker brick. To best withstand the action of these destructive agents, the most desirable brick to use is one that is as dense as is consistent with freedom from cracking and spalling with the temperature changes encountered. Practical experience has shown that soft-fired, porous brick are much more apt to become brittle, weak, and crumbly, with tendencies toward disintegration, when used as top checkers, than the harder fired, denser brick. A compact outer surface is therefore the best protection against rapid deterioration, provided spalling or cracking does not take place.

Superficially deposited carbon, so far as can be determined, has not been particularly harmful to checker brick unless it becomes so heavy as to close up the air spaces between the brick, thus interfering with or shutting off the path of travel of the gases in the checkers. Also since carbon is a poor conductor of heat, such heavy deposits may become a serious hindrance to the heating up of the checker brick, for unless the carbon is sufficiently ignited to burn away, the brick will not heat up readily.

4. Interest in Heat-Transfer Properties of Refractories

The various requirements discussed apply in the greatest degree to a rather small percentage of the total number of checker brick used where rigid conditions demand special consideration. The chief purpose of the checker brick is to provide a rapid absorption and storage of the heat traveling from the combustion zone so that they may be able to utilize this heat for the conversion of oil to gas when the process is reversed. The heat-transfer properties of various fire brick have therefore more recently attracted a large amount of interest.

This interest was largely stimulated by the results obtained by the Pacific Gas and Electric Company in one of their small generators when using Carborundum brick as checkers. At one of their small plants increased gas capacity was a quick necessity; so a small generator, one less than four feet in diameter, was checkered with Carbofrax brick instead of the usual fire brick, whereupon greatly increased gas capacity was secured, sufficient to relieve the immediate shortage of gas. Some other factors had been changed somewhat, so no exact figures were available as to the direct increase in capacity secured through the use of these brick. About one cubic foot of gas per brick per minute was secured, which was considered to be an outstanding event in gas manufacture. The brick remained intact under several months' operating conditions, the upper course only showing some deterioration by having rounded corners and edges.

Another factor arousing interest in the possible use of refractories with greatly improved heat-transfer properties as compared with average fire brick in the relation of these properties to increased gas-making capacity is that of climatic conditions. Owing to the peculiar weather conditions on the Pacific Coast, particularly in southern California, the peak winter load demand is confined to a few months—

in fact some years to a few weeks—as compared with the long winters in other parts of the country. Thus at the plant of the Los Angeles Gas and Electric Corporation there are at the present time 42 single-shell generators ranging from 20 by 30 feet to 27 by 43 feet in size. All these generators are pressed into service, sometimes at considerable overloads, for perhaps only a few weeks of the coldest weather when the heavy demand for gas must be supplied. One-half to two-thirds of the generators are more or less intermittently in operation for about 4 months, while the rest of the year the demand is supplied by 4 to 8 generators. With the rapid growth of these communities the peak demand for gas (of short duration), constantly increases, so that the ratio of excess generators that have to be built, idle most of the time, correspondingly increases. If, however, increased gas-making capacity can be secured by the use of checker brick of superior thermal properties, even at greatly increased initial costs of the brick, the necessity of building a large number of excess generators would be largely relieved. Refractories of high initial cost must have a long life in the generator, however, as well as superior thermal properties, in order to justify their use.

5. Heat Transfer in a Generator

The transfer of heat from the hot gas to the brick and from the brick to the cold oil and gases takes place by the usual three ways: radiation, convection, and conduction. Except for the presence of soot and carbon, the transfer of heat by radiation is very small, since the surface resistance of the gases is small. Transfer of heat by convection is probably not an important factor owing to the fact that the average temperature of the brick surface is lower than that of the hot gases passing by during the heat period, while during the make period the reverse is true, so that the two tend to equalize each other. Conduction is the most important factor, since the transfer of heat from the gases to the brick, from the brick to the oil, steam, and gas, as well as from the surface of the brick to its interior, takes place by conduction. Thermal conductivity is, therefore, an important property of the checker brick.

6. Thermal Conductivity of Refractories

Although many factors affect the thermal conductivity value, such as the raw materials used, impurities present, method of manufacture, density, temperature of firing of the brick to be tested, as well as the temperature of conductivity measurement, accuracy of thermal-conductivity apparatus, and methods used in making the determination, the most important of the factors mentioned in the practical application of the refractories to checker use are those of temperature of the conductivity measurement and density of the brick. Because of these many variable factors and the difficulty in making true coefficient-of-thermal-conductivity measurements, the multiplicity of thermal-conductivity values that have been obtained is confusing. A search of the available literature reveals a large number of thermal-conductivity values for various refractories that are not only very confusing but contradictory in many instances. It then becomes very difficult to select conductivity values for heat-transfer calculations; and yet accurate thermal-conductivity values are of far-reaching importance in their influence on heat transfer and calculations of problems connected therewith.

The consensus of opinion of many investigators on the thermal conductivity of refractories is that the greater the density of the brick the higher is its heat conductivity, so that apparent density serves as a crude index of the conductivity. It appears, therefore, that a dense checker brick is much to be preferred, not only because of its resistance to deterioration with use in the generator, but also because of its superior thermal conductivity and superior heat-transfer properties. In accordance with these views particular attention is now being paid to this type of checker brick. Much denser and harder fired fireclay checker brick are now under trial in generators in order to determine their resistance to spalling and disintegrating influences, since there is some doubt as to their ability to withstand the operating conditions as well as the more open porous type. Although not having been particularly realized in the past, it is now recognized that whatever can be done to increase the density and heat conductivity of the checker brick will increase its value in use.

Since the conductivity of a refractory is not the same at all temperatures, usually increasing with increase in temperature, thermal conductivities of refractories at the higher temperatures are of special interest. There is, however, a scarcity of data on the thermal conductivity of various refractories at the higher temperatures, particularly above 1500°F, or at oil-gas generator temperatures, so that much remains to be done in this connection.

7. Diffusivity of Refractories

The rate at which heat is stored up in a brick depends not only upon its thermal conductivity but also upon its diffusivity, density, and specific heat, as well as upon the thickness, shape, and dimensions of the brick. Since conductivity values alone apply only when the heating is constant over a prolonged period so that a state of equilibrium is reached, which is not the case in the generator with its operating cycles, the conductivity must be divided by the product of the apparent density and specific heat in order to show the extent to which the heat will be diffused through the checker brick. Since the rate of heating of the interior of the brick is proportional to the factor $\frac{\text{conductivity}}{\text{specific heat} \times \text{density}}$, or diffusivity constant, it largely determines how much heat will be stored in a brick in a given time, and is therefore of great importance.

High thermal conductivity and high diffusivity (and therefore high density and high specific heats) are consequently all very desirable in checker brick in gas generators where the cycles of heat-to-make and back again are rapid. The importance of high density has already been considered, which applies equally well to the apparent density. Specific heats of various refractories, particularly at the higher temperatures, are not generally available, however. In fact, the scarcity of specific-heat determinations on refractories at high temperatures is much more pronounced than that of thermal conductivities. But here also accurate knowledge of specific heats is necessary for accurate heat-transfer calculations. In view of the importance of these constants to all the industries using regenerators, or the regenerating principle, this subject is one worthy of considerable attention by the Refractories Division of this SOCIETY, the American Refractories Institute, and others interested. A more accurate knowledge of the variables influencing the specific heats, as well as the determination of the numerical values themselves, would be of great benefit to the users of these refractories in their efforts to predict beforehand what such refractories used as checker brick would do when placed in actual service. The Mellon Institute has recently made a beginning in this direction in its work on refractories for use in regenerators, but much more data is desirable.

8. Heat Capacity and Heat Absorption of Various Refractories

The heat capacity of a brick represents the maximum amount of heat that it will absorb, which depends upon its density, specific heat, surface area, thickness, and the temperature difference of the brick surface and its initial temperature. The heat capacity per degree temperature difference per unit area of a fire brick is equal to its apparent density times its specific heat times the brick thickness when heated from all sides. It therefore determines the quantity of heat that a brick is capable of absorbing. Obviously high heat capacity, possessed to a fairly high degree by fire brick, is a very desirable property in checker brick.

Theoretically the time required for any brick to attain a constant uniform temperature is infinite. The heat flow is extremely slow, however, as the brick approaches saturation. The time required to absorb a given proportion of the maximum amount of heat possible can be calculated, as has been shown by O. A. Hougen.[1] Thus, Prof.

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[1] O. A. Hougen and D. H. Edwards, "Heat Transfer," *Chem. Met. Eng.*, **29**, No. 18, October, 1923.

Hougen's series exponential formula can be used to calculate the amount of heat absorbed by various refractories per unit area at various time-intervals when heated from two sides at a constant temperature. The most desirable time-interval between gas reversals for checker brick of given material and thickness can thus be obtained. Additional calculations, as shown in the article cited, can be applied to give the total heat absorbed per unit volume and for the total volume of the generator. This total heat is dependent upon the heat capacity of the brick used, the thickness of checker wall, spacing between bricks, and the nature of the checker-brick construction.

Although some improvements can be made in the gas-making capacity of fireclay brick by increasing density, refractoriness, etc., yet the possibilities in the use of other types of brick which are superior in one or more heat-transfer properties are being investigated. Such refractories as silica, magnesite, zirconia, bauxite, diaspor, chrome, as well as the super-refractories: Carborundum, fused magnesia, fused spinel, and fused alumina, are all available for consideration. Since all are more costly than fire clay, the super-refractories very much so, their use appears to be limited to those purposes where they will give far superior service. Of these, zirconia, diaspor, and bauxite brick have a lower conductivity than fire clay, without greatly increased heat capacities, which, combined with their cost, does not make them particularly attractive. Chrome brick are costly; no figures are available as to their specific heat, and the thermal conductivity is not accurately known, except that the conductivity is higher than that of clay and lower than that of magnesite brick. It is therefore difficult to consider their value in this connection. This leaves magnesite, silica, and the super-refractories for active consideration.

In a paper[1] presented at the 32nd Annual Convention of the Pacific Coast Gas Association, Portland, Oregon, August 17–21, 1925, the writer assembled some data on the thermal properties of these various refractories, based on the best data available and on general averages in some cases. These thermal properties, at an average temperature of 1700°F, are given in Table I. The heat capacity values and the time required to reach 95% saturation, which time represents the longest desirable period for reversal of the cycle, are given in Table II and are based upon calculations made by the use of the formulas in the article[1] by Profs. Hougen and Edwards. The values in Table II are also plotted in Figs. 3 and 4. The longest desirable period for reversal applies particularly to the heat period, since the make period is governed largely by the rate of gas manufacture during the cycle.

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[1] H. J. Knollman, "Some Refractories Problems in the Oil Gas Industry," *Proceedings Pacific Coast Gas Association* Vol. 16, 1925.

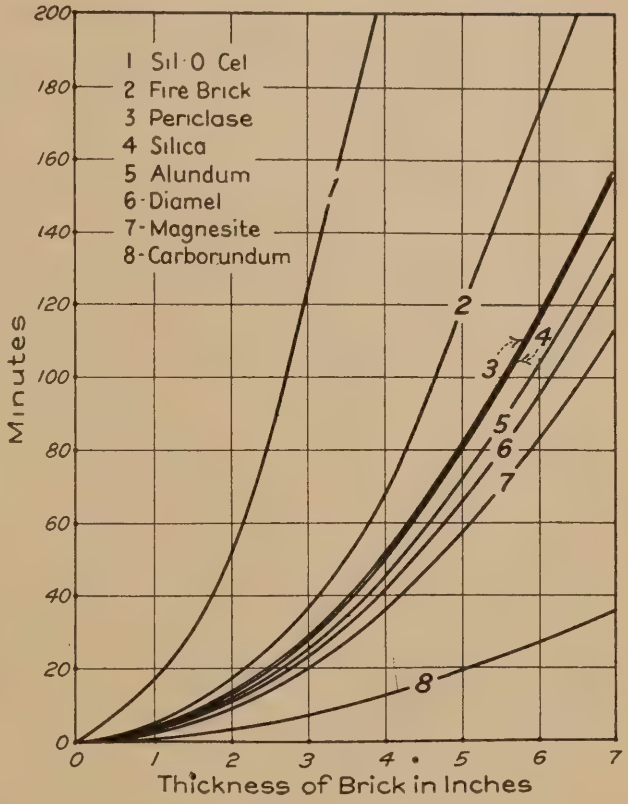

FIG. 3.—Time required to heat refractories of various thicknesses to 95% saturation.

Figure 3 shows the time required to heat refractories of various thickness to 95% saturation; Fig. 4 shows the heat absorbed by various refractories 2½ inches thick at various time-intervals when the average temperature is 1700°F. The curves vary considerably, depending upon the constants listed in Table I. Sil-O-Cel appears on these curves in order to show its value as an insulator and why it should be avoided for checker use, even if it were refractory enough for such use. These values have their limitations, not only because of lack of accurate knowledge as to their conductivity, specific heat, the average temperature assumed, and the variation in these properties with temperature, but the heat-flow calculations are also affected by the heat-transfer coefficient of gas to brick, the surface resistance of the gas film in contact with the brick, and by the assumption that the heat is flowing in from two parallel sides only, an assumption very nearly, but not strictly, true. The values obtained, however, represent relative values of the various refractories with regard to their different thermal properties so that some predictions as to their probable action in their relation to the manufacture of gas can be made.

TABLE I

THERMAL PROPERTIES OF REFRACTORIES

Material	Conductivity Gm/cal/sec/units	Apparent density	Specific heat	Heat capacity per unit volume per degree temp. diff.	Diffusivity
Fire brick	0.0034	1.905	0.245	0.467	0.0074
Silica	0.0040	1.56	0.265	0.413	0.0097
Magnesite	0.0095	2.60	0.273	0.710	0.0134
Periclase	0.0080	2.80	0.290	0.812	0.0099
Alundum	0.0065	2.45	0.250	0.612	0.0106
Carborundum	0.0258	2.45	0.228	0.559	0.0466
Diamel	0.0075	2.30	0.275	0.633	0.0119

TABLE II

HEAT CAPACITIES AND TIME REQUIRED TO HEAT REFRACTORIES

Type of brick	Thickness (inches)	Heat capacity per degree per unit area. Gm/cal.	Time required to reach 95 % saturation in min.
Fire brick	1½	0.889	10.5
	2	1.186	18.7
	2½	1.482	29.2
	5	2.964	116.8
Carborundum	1½	1.065	1.6
	2	1.420	2.8
	2½	1.775	4.4
	5	3.549	17.6
Magnesite	1½	1.352	5.1
	2	1.803	9.2
	2½	2.254	14.3
	5	4.508	57.2
Periclase	1½	1.547	7.2
	2	2.062	12.8
	2½	2.578	20.0
	5	5.156	80.0
Silica	1½	0.787	7.1
	2	1.049	12.7
	2½	1.311	19.8
	5	2.622	79.2
Alundum	1½	1.166	6.4
	2	1.554	11.4
	2½	1.943	17.8
	5	3.886	71.2
Diamel (Fused Magnesia Spinel)	1½	1.205	5.9
	2	1.607	10.5
	2½	2.008	16.4
	5	4.016	65.6

9. Thermal Properties of Various Refractory Types

Silicon-carbide brick have a very high conductivity and diffusivity, and the time required to reach heat saturation is very much shorter than for any other refractory type. According to the results in Table II or Fig. 3, the indicated period of reversal at 1700°F for a standard brick is only about 4½ minutes. Their heat capacity is limited, however, so that their decided advantage is in permitting rapid cycles of operation wherein a unit volume of gas may be made in considerably less time than where other brick are used. Since they are very costly, they must have a long life and freedom from deterioration for a long period of time, as well as superiority in gas manufacture, in order to warrant their extensive use. Based upon results already obtained in a small way and upon their indicated value, several thousand silicon-carbide brick have been purchased by the Los Angeles Gas and Electric Corporation and are to be given a thorough trial in a regular generator at this Company's works.

Owing to their very high heat capacity combined with high diffusivity and quite high conductivity, greatly surpassing fire brick, the magnesite type of refractories, with respect to their thermal properties, are most nearly ideal for checker use. They absorb the largest quantities of heat of any of the refractories, and the time required for a standard magnesite brick to reach near-saturation is approximately half of that required by fire brick. Since magnesite brick, under most conditions of use, are subject to the serious defects of excessive cracking and spalling, and to disintegration when in contact with steam, their practical use is in doubt at present. Also, their much greater initial cost over fire brick, especially the fused magnesia brick, is an important item. Since the temperatures in the checker-brick section in general are not excessive and the temperature fluctuations are moderate, generally ranging from 100 to 500° per cycle, it appears as though they may be successfully applied to this use. In order to determine this point, a few representative magnesite brick have been placed in representative locations in a generator and are in use at the present time. No report as to their action is as yet available.

Fused magnesia spinel and fused alumina brick appear to have the required stability, are lower in conductivity and diffusivity than silicon carbide and the magnesite type, but are considerably higher in these properties than fire brick. They are very expensive, but appear attractive because of their stability and excellent thermal properties. The time required for them to reach near-saturation is but slightly over the 15-minute heating cycle now used by a number of the plants in operating their generators, while the time required for a standard 9-inch fire brick is about 29 minutes, nearly double the heating period now used. Because of the longer period of reversal of these brick as compared with silicon carbide, longer operating cycles are indicated, but greater heat storage capacity is obtained by their use as compared with silicon carbide. Several thousand fused magnesia spinel brick have been obtained for use in a generator in order to determine their efficiency in gas manufacture. A few representative fused alumina brick are also being given a trial.

Silica brick have higher conductivity, specific heat, and diffusivity than fire brick, require less time to reach heat saturation, but on account of their low apparent density, have a somewhat lower heat capacity. Owing to the fact that the standard 9-inch brick, according to these figures, require but 20 minutes to reach the desirable period for reversal, as compared with nearly 30 minutes for fire brick, their use is advantageous, provided they remain intact. Owing to their spalling tendencies and sensitiveness to temperature changes, their use also is in doubt. Particularly is this true for generators in intermittent operation, owing to fluctuations in the demand for gas. By slow initial heating up, and by keeping the temperature cycles above 1000°F, it appears that their use would be practical. As in the other cases, a few representative silica brick have been placed in a generator in order to determine their stability under operating conditions.

Critical observation of Tables I and II and of Figures 3 and 4 shows that all the refractories there given are superior to fire brick in one or more of the thermal or heat-transfer properties. Thus fire brick is the lowest in conductivity, diffusivity, and time required to reach 95% saturation. Only silica brick have a lower density and heat capacity than fire brick, while only silicon-carbide brick have a lower specific heat.

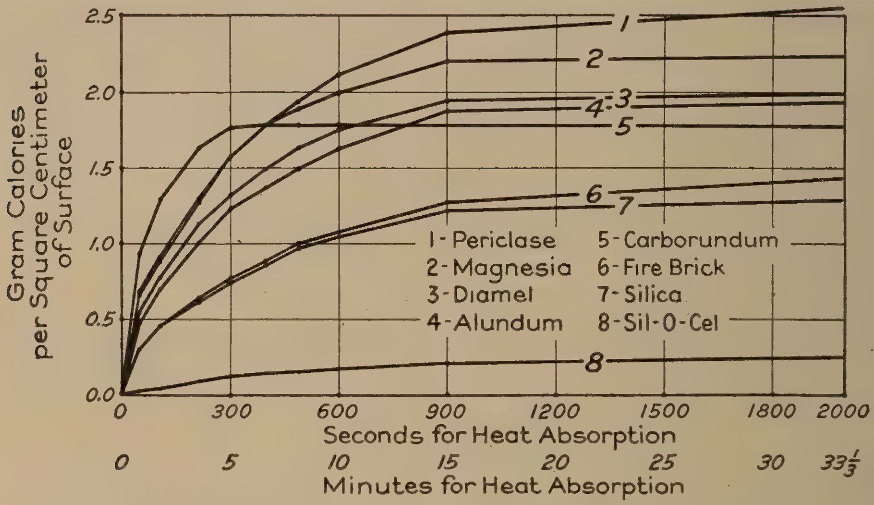

FIG. 4.—Heat absorbed by various refractories 2½ inches thick. Average temperature 1700°.

The extensive use of these refractories is problematical at the present time owing either to their very greatly increased cost or to some marked inherent physical weakness. It therefore is necessary to study the other factors involved in generator checker construction, such as the heat-transfer coefficient between gas and brick, thickness of checker brick used, spacing between checkers, and the proper height of checkers in a generator of given size.

10. Heat-Transfer Coefficient of Gas to Brick

The coefficient of heat transfer, closely related to conductivity, but independent of the kind of refractory used, varies considerably in value, and it determines the rate of heat transfer from the gases to the brick surface. It is dependent upon the temperature of the gases, their density and velocity, size and shape of checker flues. The larger the coefficient the greater is the transfer of heat from the gases to the brick and vice versa. The heat-transfer coefficient in general grows with the velocity of flow of the products of combustion, so that proper checker spacing is of importance. The value of the coefficient is rather low in generators of average size and average checker spacings, approximations giving a value in the neighborhood of 2.0. It is a difficult constant to determine accurately, but approximate values can be calculated and are of value in determining the necessary amount of heating surface required.

11. Influence of Checker-Brick Height, Thickness, and Flue Spacing

The proper ratio of height of checker brick to heating surface, which permits the greatest increase in heat exchange between the brick and the oil vapors and gases, is not accurately known. Greater ease in uniformity of temperature control from top to bottom checkers is obtained by decreased checker heights. Increased checker heights, especially with close checker spacings, also tend to cut down the velocity of the gases passing by, so that the heat-transfer coefficient of gas to brick is then decreased. Following this line of reasoning, low wide generators appear preferable to the longer narrow ones, but exact limits have not been determined.

The size of checker brick and the spacings between them, determining the size of the checker flues, have an influence on their efficiency. The relative size of brick and checker spacing must be governed by the fact that the arrangement must be such as to offer a maximum area for absorption of heat and a minimum retardation to gas flow, combined with structural strength and durability.

In a given generator with constant checker openings, increased brick thickness increases the cubic feet of brick work in the checkers and weight of brick used. There is a decrease in the space occupied by air or gas, the number of brick used, the number of checker openings, area of these openings, and the heating surface of the checker brick. The ratio of heating surface to cubical contents of brick work is thus lowered by increased brick thickness.

From Table II or Fig. 3, the advantages of using thin fire brick in preference to the thick brick is readily seen, when the heat period of the oil-gas-process cycle is from 10 to 15 minutes. Since the time required for various thicknesses of brick to absorb a given proportion of its maximum heat varies as the square of the brick thickness, brick of relatively low conductivity and diffusivity such as fire brick should be thin for short cycles of heating and cooling. Brick of high conductivity and diffusivity, such as Carborundum, can be used to advantage in the thicker sizes. The use of fire brick thinner than the standard 2½-inch is therefore warranted as long as the stability and structural strength of the checker work is not impaired, so that even the use of a 2-inch brick is advantageous. Less time is required for heat saturation and there is less lag between the outside skin surface and the interior of the brick with rapid temperature fluctuations and quick cycles. The center of thin brick is therefore more perfectly utilized, although the total heat capacity is lower for the thinner brick.

Theoretically the checker openings should be as small as is consistent with proper gas flow and freedom from danger of excessive carbonization. In a given generator with constant thickness of brick, increased size of checker openings increases the space occupied by air or gas, the area of checker openings, and the ratio of heating surface to cubical contents of brick work. There is a decrease in cubic feet of brick work, number of brick used, number of checker openings, heating surface of checker brick, and weight of brick work in the checkers. The flue spaces must be kept large enough, however, to safeguard against the retardation of gas flow by friction, so that the proper velocity may be maintained.

12. Gas Manufacture By-Products

These are some of the main factors that have to be considered in the use of checker brick in their relation to gas manufacture. The chief undesirable by-products in gas manufacture are carbon, naphthalene, and tar. Large quantities of carbon or lampblack especially are formed. It appears likely that refractories of increased thermal conductivity, especially the crystalline types, will tend to reduce the amount of carbon formed or remaining in the checkers, owing to their ability to rapidly absorb and give up heat. There have been indications that less carbon is formed by the use of Carborundum brick already tried out. The reduction in the amount of the low temperature by-products formed is likely on account of the greatly increased heat capacity of such refractories.

Although the considerations enumerated with regard to the heat-transfer properties of various refractories in their influence upon the conversion of oil to gas in this industry are still in the experimental stage and largely theoretical, they are given in this paper to show the trend of research in refractories by the oil-gas industry on the Pacific Coast. The actual application of the refractories other than fire brick in the industry involves so many variables and so many probable changes in generator operations that a large amount of research is necessary to determine the proper refractories to use as checker brick on the lowest cost-plus-service basis. The changes in generator operation dare not be of such a nature as to alter materially the B.t.u. value, specific gravity, chemical analysis, etc., of the gas made, so that this also must be considered in any checker brick research work.

The oil-gas industry on the Pacific Coast, in coöperation with the California Gas Research Council, is prepared to go to considerable lengths, however, in order to determine the efficiency of various refractories for gas manufacture. If the refractories of superior thermal properties are not practical to use, either on account of excessive cost or inability to withstand operating conditions, a fireclay brick approaching these properties as nearly as possible is the choice. This appears to be as dense a brick of requisite refractoriness as is consistent with freedom from spalling, cracking, and the like, because of its greater conductivity and heat capacity as compared with the softer, more porous fire brick. Also the use of as thin a brick as is consistent with structural strength and durability of the checker work is indicated, since heat saturation is then reached much more quickly.

The confusion existing at the present time as to the thermal conductivities and specific heats at the higher temperatures of the various types of refractories, as well as the total lack of data in many cases, makes it difficult to determine with a sufficient degree of accuracy needed heat-transfer data by which predictions can be made as to their probable use in the regenerative types of processes. Although difficult, the need for systematized work along these lines is evident. The choice of these constants has a material influence on the values obtained in various heat calculations, so that this appears to be a fruitful field for continued investigations on refractories and one worthy of consideration by the Refractories Division of this SOCIETY. The subject is so large that close coöperation between the various interested consumers and manufacturers of refractories would undoubtedly offer the best ultimate solution.

LOS ANGELES GAS AND ELECTRIC CORPORATION
LOS ANGELES, CALIF.

CORRECTIONS

In the paper by A. E. R. Westman and W. W. Pfeiffer, "A Comparison of the Uniformity of Strength and Texture of Fire Brick Made by Different Manufacturing Processes," *Jour. Amer. Ceram. Soc.*, 9 [9], 626–32 (1926), the arrows in Tables III and IV, pp. 630–31, are pointing in the wrong direction. They should point downward in both cases. On page 627, line 37, the word "heat" should be "head"; the phrase should read, "a pressure drop of 1 cm. water head (4°C)."

Heavy Clay Product Manufacturers Annual Meeting

February 8-12

Canadian National Clay Products Association, Toronto, Ontario

February 14-19

AMERICAN CERAMIC SOCIETY
Book-Cadillac Hotel, Detroit, Mich.

February 21-26

Common Brick Manufacturers Association, Sherman Hotel, Chicago, Ill.

These meetings were thus purposefully scheduled that those desiring to attend may route their trip with the least time and money expenditure

Seven Meetings In One

at the

AMERICAN CERAMIC SOCIETY

Meeting

One and one-half excursion concession has been granted by all the rail passenger associations

CORRECTION ON 1926 ANNUAL AUTHOR INDEX[1]

The names of the authors and titles of their paper for the August issue of the *Journal* were inadvertently omitted from the Author Index as it appeared on pages 889 and 890 of the December 1926 *Journal*. Kindly attach the following to those pages of the index.

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[1] See pages 889 and 890 of December *Journal*, 1926.

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